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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of an epoxy resin constituent suitable as a resin constituent for fiber strengthening composite material. In more detail, also in low-pressure molding, it excels in surface smooth nature and is related with the manufacture method of a resin constituent of giving good mold goods without a surface pit.

[0002]

[Description of the Prior Art] The fiber strengthening composite material which consists of strengthening fiber and a matrix resin is broadly used for various industrial ways, the sport use, the aerospace use, etc. from the outstanding dynamics property etc. The demand property over fiber strengthening composite material is becoming still severer as the operating experience is gained in recent years. In order to fully pull out the dynamics property and endurance of fiber strengthening composite material, while lessening the defect which leads to on-the-strength reduction like porosity (opening), there is a demand which asks for the smooth nature on the front face of a Plastic solid. If a polish process is needed before paint and a pit exists when the front face of a Plastic solid is coarse, moisture will become easy to permeate from there and the problem of reducing the physical properties of the base material itself or other base materials which were stuck and united will be caused.

[0003] Especially an on-the-strength fall according [on industrial use and the structural material for aircrafts and] to water absorption can grow into a fatal problem on safe. Here, it is thought that the factor which influences the surface smooth nature of a Plastic solid is in the following two points. One of them depends on the composition of a prepreg, and a form. Namely, although a prepreg consists of a resin constituent and strengthening fiber, as for the moldings of a textile prepreg, surface [, such as a surface pit,] smooth nature is easy to be spoiled rather than the moldings of a 1 directivity prepreg, for example. It is for a resin deficit to tend to take place to the irregularity of the textile confounding section, and the eye omission section. Recently, the prepreg with few resin contents is demanded from the demand to the further lightweight-izing. Generally, since the irregularity on the front face of a Plastic solid tends to become large when there are few resin contents, it can be said that the expectation for the Plastic solid which makes the former rub and has surface smooth nature is great.

[0004] Moreover, the pressure at the time of fabrication is mentioned as the second factor which influences surface smooth nature. For example, a honeycomb sandwich panel is in one of the Plastic solids which the surface smooth nature of a moldings is easy to be spoiled. Although this is manufactured by the method of carrying out the laminating of the prepreg to both sides of the honeycomb core which consists for example, of aramid paper, and carrying out a vacuum forming with an autoclave, in order to prevent not being monotonous (from the hexagon cavity where a honeycomb-structure object is regular to composition), and crushing of a honeycomb, it can be called factor to which restrictions that a high pressure is not put by the well worsen surface smooth nature. Since a pressure cannot be easily applied especially to the skin panel which consists of a prepreg of the upper and lower sides of a hexagon cavity, it is easy to produce irregularity on a front face. Furthermore, the smooth

nature on the front face of a Plastic solid is that an important thing does not remain only in it but the porosity inside a skin panel has high functionality. That is, near the resin deficit section under a Plastic solid, a pressure cannot be applied easily, and it is thought that it has a bad influence also on generating of internal porosity.

[0005] As a method of improving surface smooth nature, the resultant of the liquefied butadiene acrylic nitrile rubber and epoxy resin which have a carboxyl group is used for both ends, and the manufacturing method of a hot adhesive property and the honeycomb sandwich panel which does not have a defect in a moldings front face is indicated by JP,58-82755,A. Moreover, the manufacturing method of a hot adhesive property and the honeycomb sandwich panel which does not have a defect in a moldings front face is indicated by JP,61-29613,B with the epoxy resin constituent of the epoxy resin which has a diglycidyl amino group, and the liquefied butadiene acrylic nitrile rubber which has a carboxyl group in both ends. Furthermore, the specific epoxy resin constituent containing a dicyandiamide and a dimethyl urea compound is indicated by JP,58-167625,A as a method of obtaining the composite which does not have a void and a crack in low-pressure molding. However, neither of the methods can be said that the surface smooth nature of a Plastic solid is enough. Moreover, in JP,5-239317,A and JP,6-25446,A, there is a publication which uses the high resin of thixotropy nature for the textile prepreg for HANIKA mucosures. However, although the viscosity in 80 degrees C uses the hyperviscous resin of 5000poise or more therefore, there is another problem that a resin streak cannot produce a prepreg easily deficiently. In which method described above, it was not what has an effect enough in the surface smooth nature which is excellent in internal porosity and is made into the purpose by this invention.

[0006]

[Problem(s) to be Solved by the Invention] The technical problem of this invention prevents the pit not only on the porosity inside a panel but the front face of a Plastic solid, and generating of the resin deficit section, and is to offer the manufacture method of the resin constituent for fiber strengthening composite material that the good Plastic solid of surface smooth nature can be manufactured.

[0007] Moreover, while it has the good tuck nature and drape nature which make a matrix resin the resin constituent of the above-mentioned this invention and the handling on fabrication offers an easy prepreg, further, it excels in thermal resistance, a compression property, and shock resistance, and is in offering a Plastic solid suitable as a structural material.

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the manufacture method of the resin constituent for fiber strengthening composite material of this invention is faced manufacturing the epoxy resin constituent which consists of an epoxy resin, an inorganic particle, a butadiene acrylic nitrile rubber, and a curing agent as a resin constituent for fiber strengthening composite material, and consists of a method characterized by passing through the process which makes a part of epoxy resin distribute an inorganic particle beforehand.

[0009] In the above-mentioned method, the process which distributes an inorganic particle to a part of epoxy resin is called master-ization. In this invention, it is important to use the master-ized inorganic particle constituent, and if powder addition is carried out without master-izing, a result which spoils surface smooth nature will be brought. After the differential powder in the inside of an epoxy resin fully carries out churning mixture of the liquefied epoxy resin for these inorganic particles in an inorganic particle and ordinary temperature, it can attain easily by passing a close clearance part like 3 rolls.

[0010] Thus, the good Plastic solid of surface smooth nature can be manufactured by mixing the master-ized inorganic particle mixture resin with an epoxy resin and a curing agent, and considering as the epoxy resin constituent which rationalized viscosity.

[0011]

[Embodiments of the Invention] The form of desirable operation of this invention is explained in detail below. The epoxy resin which uses as a precursor the compound which has amines, phenols, and a carbon-carbon double bond especially as an epoxy resin suitable for this invention is desirable. Specifically, the various isomers of a tetraglycidyl ether amino diphenylmethane, triglycidyl-para aminophenol, and triglycidyl amino cresol are mentioned as a glycidyl amine type epoxy resin which

uses amines as a precursor. Since a tetraglycidyl ether amino diphenylmethane is excellent in thermal resistance as a resin for composite material as aircraft structure material, it is desirable.

[0012] As an epoxy resin which uses phenols as a precursor, novolak type epoxy resins, such as bisphenol type epoxy resins, such as the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, and a bisphenol S type epoxy resin, and a phenol novolak type epoxy resin, a cresol novolak type epoxy resin, and a resorcinol type epoxy resin are mentioned. Since the liquefied bisphenol A type epoxy resin and a bisphenol female mold epoxy resin are hypoviscosity, it is desirable to blend with other epoxy resins as an additive.

[0013] Moreover, although these epoxy resins may be used independently, it is good to blend suitably and to use. For example, since the combination of a glycidyl amine type epoxy resin and a glycidyl ether type epoxy resin has good thermal resistance, water resistance, and workability, it is desirable. It is desirable to mix 30 - 60 weight section and a bisphenol type epoxy resin for a glycidyl ether type epoxy resin, to mix 0 - 30 weight section for 40 - 80 weight section and a novolak type epoxy resin, and to use especially.

[0014] In this invention, although an inorganic particle is used in order to give the surface smooth nature of a Plastic solid, talc, an aluminum silicate, a particle-like silica, a calcium carbonate, a mica, a montmorillonite, carbon black, silicon carbide, a hydrated alumina, etc. are mentioned as an example of this inorganic particle. What has a particle diameter 50 micrometers or less is desirable still more desirable, and these inorganic particles can use a thing 20 micrometers or less. A particle-like silica has the effect which raises the viscosity of an epoxy resin solution, and the especially greatly desirable effect of improving the flow property of a resin, especially. As a particle-like silica which makes a silicon dioxide a basic frame, what the average of primary particle size has in the range of 5-40nm is marketed with the tradename of "Aerosil" (product made from Japanese Aerosil). As a specific surface area of this particle, the thing of the range of 50-400m² / g is desirable. Moreover, it is more desirable to use the hydrophobic particle-like silica which replaced the hydrogen of a silanol group with the methyl group or the octyl machine, although that by which the front face of a silica is being worn by the silanol group is generally used from the field it the effect of improving the surface smooth nature of a resin is not only high, but improves the field of viscosity stabilization and the water resistance of mold goods, and the dynamics property represented by compressive strength.

[0015] An inorganic particle passes through the process which a part of epoxy resin is made to distribute beforehand in this invention. Master-ization can be attained by passing a close clearance part like 3 rolls, after fully carrying out churning mixture of the liquefied epoxy resin in an inorganic particle and ordinary temperature.

[0016] As an epoxy resin used for master-ization, the thing of the range of 100-300 is preferably used for a weight per epoxy equivalent in ordinary temperature. The epoxy resin of a liquid is desirable, for example, bisphenol type epoxy resins, such as the bisphenol A type epoxy resin, a bisphenol female mold epoxy resin, and a bisphenol S type epoxy resin, and a glycidyl amine type epoxy resin are used. Moreover, although these liquefied epoxy resins may be used independently, it is good to blend suitably and to use.

[0017] Thus, compared with the case where did not master-ize but an inorganic particle is used as it was, the surface smooth nature of a Plastic solid becomes a remarkable good thing by mixing with an epoxy resin the inorganic particle which master-ized and carried out differential powder. One of the differences in these both resin constituent appears in the viscosity property of the epoxy resin constituent which used each inorganic particle. Although the viscosity of the epoxy resin constituent which generally obtains the good Plastic solid of surface smooth nature is in the range whose viscosity in 80 degrees C is 100-1000poise and the minimum value of the viscosity of the resin constituent in temperature up process is in the range which is 10-300poise Here, if the master-ized inorganic particle is used, compared with the resin which does not add powdered addition or a particle at all, the viscosity of 80 degrees C - nearly 120 degrees C will be high, and it will be small temperature-independent.

[0018] If the resin constituent whose minimum viscosity [in / less than 100poise or temperature up process / in the viscosity in 80 degrees C] is less than 10poise is used If there are surface smooth nature

and an inclination for generating of the porosity inside a Plastic solid to increase and the resin constituent with which the viscosity in 80 degrees C exceeded 1000poise, or the minimum viscosity exceeded 300poise on the other hand is used The fluidity of a resin runs short, it is [film-] hard to use, and there is an inclination for the impregnating ability to strengthening fiber to become bad.

[0019] Thus, if the master-sized inorganic particle is used, the flow property at the time of fabrication of an epoxy resin will be improved, smooth nature will also be given to the crevice which pressures, such as a Plastic solid of a honeycomb and a textile prepreg, cannot require especially easily, and the inclination decreasing [internal porosity's] will become remarkable.

[0020] Although inorganic particle addition has the effect which pushes up the minimum viscosity value, combined use of a butadiene acrylic nitrile rubber with the effect which carries out piling of the whole viscosity is suitable in order to raise the surface smooth nature of a Plastic solid and the flexibility of a prepreg, and adhesiveness further. It is desirable to add reactant machine content solid acrylonitrile-butadiene rubber especially in addition to the above-mentioned epoxy resin. Reactant machine content solid acrylonitrile-butadiene rubber is hyperviscous rubber which does not have a fluidity at a room temperature, and is rubber which has the Mooney viscosity in 100 degrees C more specifically measured by JIS-K6300 in the range of 20-100. Liquid rubber is deficient in the effect which raises matrix-resin viscosity compared with solid rubber, and since it is necessary to add so much, it tends to check thermal resistance. The epoxy resin constituent which added reactant machine content solid acrylonitrile-butadiene rubber here serves as a suitable matrix resin to obtain the good prepreg of adhesiveness and flexibility. In case the adhesiveness of a prepreg or flexibility which are acquired may not become enough if the Mooney viscosity in 100 degrees C of this rubber is too small, the viscosity of an epoxy resin constituent will become high if too large, and it is made a prepreg, the impregnating ability to strengthening fiber may be spoiled.

[0021] As a reactant machine, a carboxyl group, the amino group, an epoxy group, etc. can be illustrated. If it becomes, since the adhesive property with the rubber phase which carried out differential powder to the hardened resin phase for which it does not have the reactant machine into it is low, the dynamics property of the matrix resin after hardening may fall. The addition of solid rubber which has a carboxyl group or the amino group with high reactivity with an epoxy resin especially is desirable. As solid acrylonitrile-butadiene rubber which has a reactant machine, commercial elegance, such as NIPPORU (registered trademark) 1072 by Nippon Zeon [Co., Ltd.] Co., Ltd., can be used.

[0022] Here, the weight rate for which it accounts to the good inorganic particle of the surface smooth nature of a Plastic solid and the whole solid butadiene acrylic nitrile-rubber resin constituent has 0.8 - 5 % of the weight, and 2 - 5% of the weight of a desirable range respectively. If there are few loadings of reactant machine content solid acrylonitrile-butadiene rubber than 2 % of the weight when there are few inorganic particles than 0.8 % of the weight and, it will be easy to become what not only the surface smooth nature of a Plastic solid is inferior, but was inferior in the adhesiveness of the prepreg obtained, or flexibility. On the other hand, if there are more loadings than 5 % of the weight, resin viscosity becomes high and the impregnating ability to the strengthening fiber in the case of prepreg-izing may be spoiled. An inorganic particle is 0.8 - 3% of the weight of a range, and the solid butadiene acrylic nitrile rubber of a more desirable addition is 2 - 4% of the weight of a range. Here, the smooth nature of a skin panel front face becomes what was more excellent by using together an inorganic particle and a solid butadiene acrylic nitrile rubber.

[0023] Moreover, it is also possible to use it, blending thermoplastics, such as polyether sulphone, polyether imide, and a polyvinyl formal, into these epoxy resin constituents.

[0024] This can be used if it is the compound which has an epoxy group and the active group which can react as a curing agent used for these epoxy resin constituents. Preferably, the compound which has the amino group, an acid-anhydride machine, and an azide machine is suitable. For example, a dicyandiamide, a diaminodiphenyl sulfone, diamino diphenylmethanes, those various isomers, aminobenzoic-acid ester, various acid anhydrides, a phenol novolak resin, and a cresol novolak resin are mentioned.

[0025] Moreover, if an aromatic diamine is used as a curing agent, a heat-resistant good hardened

material will be obtained. Since a heat-resistant good hardened material is obtained more, especially a diaminodiphenyl sulfone and its isomer are most suitable for this invention. When using an aromatic diamine as a curing agent, it is more desirable to consider as the equivalent mostly suitably [the addition / considering as the range whose amount of the active hydrogen of a diaminodiphenyl sulfone is 0.4-1.6Eq to the epoxy group of an epoxy resin], and in stoichiometry. A dicyandiamine is used especially preferably, when it can ask for the shelf life of a prepreg more, and 0.5 - 10 % of the weight per resin constituent whole quantity is suitable for the addition.

[0026] Moreover, urea derivatives, such as 3-(3, 4-dichlorophenyl)-1 and 1 dimethylurea (henceforth, DCMU), 3-(3-chlorophenyl)-1, and 1 dimethylurea, an imidazole compound, a tertiary amine compound, etc. can be used together as a hardening accelerator. DCMU which is excellent in preservation stability especially is desirable.

[0027] Generally, since the toughness of an epoxy resin is not so high, in order to improve resin toughness, you may add thermoplastics to an epoxy resin constituent further. Specifically, they are polyether sulphone, polyether imide, a polyvinyl formal, etc. Moreover, it is desirable to also make a resin constituent contain particles, such as a core / shell polymer, for the improvement in a bond strength.

[0028] Thus, as for the viscosity of the obtained resin constituent, it is desirable that it is in the range whose viscosity in 80 degrees C is 100-1000poise, and is in the range whose minimum value of the viscosity of the resin constituent in temperature up process is 10-300poise.

[0029] Moreover, in this invention, the inorganic particle in an epoxy resin is carrying out differential powder, and when a floc 20 micrometers or more hardly exists, the surface smooth nature of a Plastic solid is improved notably. When powder addition is carried out without master-izing an inorganic particle, many flocs 20 micrometers or more may exist, and surface smooth nature may be inferior.

[0030] The resin constituent obtained by the manufacture method of this invention is combined with strengthening fiber, and is preferably used as a prepreg.

[0031] As strengthening fiber, a glass fiber, a carbon fiber, an aramid fiber, a boron fiber, an alumina fiber, silicon carbide fiber, etc. are used. Two or more sorts may be mixed and these fiber may be used. It is more lightweight, and especially in order to obtain mold goods with more high endurance, use of a carbon fiber is desirable. The high strength carbon fiber of 4.4 or more GPas of the field that the shock resistance when considering as the tensile strength and the honeycomb-structure object of fiber original is high to tensile strength is desirable. Furthermore, use of the carbon fiber the field of shock-proof improvement to whose **** ductility is 1.7% or more is more desirable.

[0032] It is not limited about the gestalt or array of strengthening fiber, for example, the continuous glass fiber which lengthened to ** and was arranged with it on the other hand, a tow, textiles (cross), a mat, knitting, a plaited cord, etc. are used. However, the thing of the ease of the dynamics property of a honeycomb-structure object and a forming process to a textile gestalt is the most desirable. Well-known 2-dimensional textiles can be conventionally used as textiles using this strengthening fiber. The 2 shaft textiles with which warp and the woof, such as plain weave, twill, and a satin, were each other interwoven with right-angled according to the fixed principle as a textile organization are desirable. Especially plain weave structure tends to build a thin Plastic solid, and it is suitable. Although the weaving yarn of textiles consists of a fiber bundle, 2,500-25,000 ranges have the desirable number of filaments in one fiber bundle. Or less in 2,500, a fiber array tends to cause an on-the-strength fall being easy to move in a zigzag direction. Moreover, or more in 25,000, resin sinking in cannot take place easily at the time of prepreg production or fabrication, and it is easy to generate porosity. They are 2,800-15,000 ranges more preferably.

[0033] In this invention, it is desirable that a resin content considers as 35 - 50% of the weight of a prepreg. When a resin content is 35 or less % of the weight, the surface smooth nature of a resin becomes bad, or tends to cause an adhesive fall with a base material. Moreover, if a resin content exceeds 50 % of the weight, since there will be a point that a resin flow tends to happen feeling uneasy, at the time of prepreg production and the weight of a Plastic solid will increase, the effect of lightweight-izing becomes small.

[0034] As the manufacture method of a prepreg, a matrix resin is dissolved in a solvent, it hypoviscosity-izes and the wet method to infiltrate and methods, such as the hot-melt method (the dry method) which hypoviscosity-izes by heating and is infiltrated, are mentioned. The hot-melt method piles up the film which coated strengthening fiber and the epoxy resin constituent on the release paper etc. from both sides or one side, it is the method of infiltrating a resin by carrying out heating pressurization, and producing a prepreg, and in order that it may tend to control the thickness of a resin content or a prepreg, it is more desirable.

[0035] Although the method of fabricating the prepreg of this invention can mention vacuum bag molding, the autoclave fabrication which used the vacuum bag, press forming, etc., in order to obtain the highly efficient structure, its autoclave fabrication is desirable.

[0036] as the honeycomb core used for the examination for checking the effect by this invention -- Showa Aircraft Industry Make "the Nomex honeycomb" -- SAH1 / 8-8.0 was used Moreover, the laminating of the laminating composition of a textile prepreg was carried out to the upper surface of a honeycomb core with the composition from which the direction of strengthening fiber becomes (**45 degree)/(0-degree / 90 degrees)/(0-degree / 90 degrees)/(0 degree / 90 degrees) from a top at order, and becomes 0 degree / (90 degree)/(0-degree / 90 degrees)/(**45 degrees) about a textile prepreg on the honeycomb-core inferior surface of tongue The temperature up of the hardening was carried out to 180 degrees C by part for 1.5-degree-C/, and it was performed within the autoclave on the conditions held by this ** for 2 hours. the state where put the nylon bag on the layered product on an aluminum tool board, and the inside of a bag was first maintained at the vacua at that time -- an autoclave -- putting in -- a degree -- 1.5 kg/cm² up to -- the place which gave the pressure -- the vacuum in a bag -- an ordinary pressure -- returning -- after that 3 kg/cm² up to -- the temperature up was performed after carrying out the pressure up

[0037] the Plastic-solid inferior surface of tongue of the surface smooth nature of the Plastic solid hardened here is random in a tool side side (inferior surface of tongue) using Mitutoyo tabulation side granularity measuring device SurfTest301 type -- it asked from the average of the maximum height (Rmax) of the chart with which the detection needle ran and was obtained over a length of 5mm about ten places

[0038] in addition, measurement conditions -- λ of the above-mentioned measuring device -- pinching -- :8 and n -- pinching -- :n -- it pinched P_c and considered as :1 and LCD/SPCtumami:Ry

[0039] Epoxy resin viscosity was measured the following condition using the RDA-II type equipment by REOMETO Rix Corp.

Operation mode : dynamic mode Oscillation frequency range: 0.5Hz (vibration frequency 3.14 r/s)
Plate composition : Parallel board (radius of 25mm)

Gap 0.83mm Programming rate : 1.5 degrees C/min The amount of distortion: Torque controlled automatically so that it might go into the range of 2 - 200 g-cm.

[0040]

[Example] Hereafter, based on an example, this invention is explained still more concretely.

(Example 1)

<Manufacture of a particle master resin> The particle silica (Degussa AG make "Aerosil" R812) 12 weight section which carried out surface treatment to the tetraglycidyl ether diamino diphenylmethane (ELM434 by Sumitomo Chemical [Co., Ltd.] Co., Ltd.) 88 weight section with the trimethylsilyl machine was mixed with the kneader at 60 degrees C for 3 hours. The particle master constituent was obtained for the mixed resin constituent through between rolls twice using 3 rolls. The 80-degree C viscosity of this particle was 120poise.

[0041] The following resin constituents were prepared using this particle master resin. As an epoxy resin, the bisphenol A type epoxy (Ep828 by oil-ized Shell Epoxy company) 30 weight section, the cresol novolak type epoxy (ESCN220 by Sumitomo Chemical [Co., Ltd.] Co., Ltd.) 20 weight section, and the carboxyl group end acrylonitrile-butadiene rubber (NIPOL1072 by Nippon Zeon Co., Ltd.) 3.0 weight section were taught to the kneader, and it kneaded at 85 degrees C for 2 hours. 20 weight sections addition of the above-mentioned master resin was carried out after lowering the temperature at

60 degrees C, it kneaded at 60 degrees C for 1 hour, and 4 and the 4'diaminodiphenyl-sulfone 27 weight section were further added as a curing agent, and churning mixture was carried out for 30 minutes. When the viscosity in 80 degrees C of this epoxy resin constituent was measured, the viscosity in 80 degrees C was 200poise, and the minimum viscosity was 90poise. A release paper is coated with this epoxy resin constituent, and resin eyes are 70g/m². The resin film was produced. This resin film was set to the prepreg machine, it performed resin sinking in from both sides of carbon fiber textiles "TOREKA" CO7373Z (eyes 193 g/m²), and the prepreg was obtained. [by Toray Industries, Inc.] As sinking-in conditions at this time, temperature is 100 degrees C and sinking-in pressures are 4 kgf/cm². It used. next, it becomes a candidate for vertical to an aramid honeycomb core (the size of a honeycomb cell is 1/8 inch and the thickness of 1/2 inch) -- as It was made order from the top by (**45 degree)/(0-degree / 90 degrees)/(0-degree / 90 degrees), and the laminating of the textile prepreg was made to the upper surface of a honeycomb core on the honeycomb-core inferior surface of tongue with the composition of 0 degree / (90 degree)/(0-degree / 90 degrees)/(**45 degrees) (an outermost layer of drum is **45 degrees to a honeycomb core). The temperature up of the hardening was carried out to 180 degrees C by part for 1.5-degree-C/, and it was performed within the autoclave on the conditions held by this ** for 2 hours.

[0042] Putting the layered product of this honeycomb core and a prepreg on the aluminum plate which covered with the fluororesin film, the layered product was packed by the nylon film, and it performed autoclave fabrication, saving under reduced pressure from a vacuum nozzle mouth. A process condition is 3 kg/cm². After heating by 1.5 degrees C of programming rates, and min and holding by 180 degrees C/min under pressurization for 2 hours, the temperature was made to lower to 35 degrees C by 2.0 degrees C in temperature fall speed, and min. The average of the maximum height (Rmax) which measured the smooth nature on the front face of the bottom (portion which touched the aluminum board) of this sandwich panel using Surftest was 12 micrometers. Moreover, the added porosity area which grinds a sandwich panel with a sandpaper and alumina powder, takes an optical microscope photograph, and is occupied in the whole bottom skin panel area was 0.1%.

[0043] (Example 1 of comparison) As an epoxy resin, it is with a powder state about the particle silica (Degussa AG make "Aerosil" R812) which carried out surface treatment with the bisphenol A type epoxy (Ep828 by oil-ized Shell Epoxy company) 30 weight section, the cresol novolak type epoxy (ESCN220 by Sumitomo Chemical [Co., Ltd.] Co., Ltd.) 20 weight section, the carboxyl group end acrylonitrile-butadiene rubber (NIPOL1072 by Nippon Zeon Co., Ltd.) 3.0 weight section, and the trimethylsilyl machine. The 2.4 weight sections were taught to the kneader and it kneaded at 85 degrees C for 2 hours. After lowering the temperature at 60 degrees C, the tetraglycidyl ether diamino diphenylmethane (ELM434 by Sumitomo Chemical [Co., Ltd.] Co., Ltd.) 17.6 weight section was added, and it kneaded at 60 degrees C for 1 hour, and 4 and the 4'diaminodiphenyl-sulfone 27 weight section were further added as a curing agent, and churning mixture was carried out for 30 minutes. When the viscosity in 80 degrees C of this epoxy resin constituent was measured, the viscosity in 80 degrees C was 130poise, the minimum viscosity was 45poise, and it was the resin constituent of low viscosity compared with the example 1. Using this resin constituent, like the example 1, the laminating of the textile prepreg was carried out and autoclave fabrication was carried out using the aramid honeycomb core. The average of the maximum height (Rmax) which measured the smooth nature on the front face of the bottom (portion which touched the aluminum board) of this sandwich panel using Surftest was 25 micrometers. Moreover, the sandwich panel was ground with a sandpaper and alumina powder, the optical microscope photograph was taken, and porosity area % of a bottom skin panel was 0.4%.

[0044]

[Effect of the Invention] using the resin constituent manufactured by the manufacture method of the resin constituent for fiber strengthening composite material of this invention -- a pit and the resin deficit section -- few -- surface smooth nature -- being good -- while -- a Plastic solid with little porosity -- it can obtain .

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the rubber constituent for treads with which may be simultaneously satisfied of the wet-proof skid nature of a tire, rolling-resistance nature, and abrasion resistance, without falling process nature in more detail about the rubber constituent for tire treads.

[0002]

[Description of the Prior Art] With rolling resistance, a part of turning effort applied to the tire with which the automobile was equipped changes to heat energy, and it generates an energy loss. The greater part of this rolling resistance originates in the hysteresis loss accompanying repeat deformation of a tread, and the hysteresis loss is greatly accepted as the loss tangent ($\tan \delta$) of the rubber constituent which used this hysteresis loss for the tread becomes large.

[0003] On the other hand, since the fuel consumption of an automobile will increase and the air pollution problem by exhaust gas will moreover be amplified if the rolling resistance at the time of a tire run is large, it is requested socially that the rolling resistance of a tire should be decreased, mpg should be cut down and an environmental problem should be solved.

[0004] If it is going to decrease rolling resistance by using the low rubber material of glass transition temperatures, such as natural rubber and a cis polybutadiene rubber, or adjusting the kind of carbon black or softener, loadings, etc. in order to reply to this request In the former, wet-proof skid nature falls remarkably, or in the latter When the microstructure of rubber was especially similar, it was very difficult to satisfy simultaneously these [which the phenomenon in which wet-proof skid nature and abrasion resistance fall is accepted, and carry out an antinomy to **] three properties.

[0005] Overthrowing this antinomy relation and holding wet-proof skid nature and abrasion resistance enough also conventionally, the attempt which makes rolling resistance small is made, for example, an organic lithium is obtained as an initiator in JP,3-252431,A, and the pneumatic tire which used for the tread the rubber constituent which comes to blend carbon black with the raw material rubber to which a glass transition temperature makes a principal component a diene system polymer -50 degrees C or more a silica bulking agent, a silane coupling agent, and if needed is proposed. Moreover, it changes into the above-mentioned diene system polymer, a rubber constituent is similarly constituted from JP,3-252433,A using the denaturation polymer which is made to carry out the coupling reaction of the activity diene system polymer which has a lithium-carbon to carbon bond at the molecule end, and the specific silane compound, and is obtained, and the pneumatic tire which used this for the tread is proposed. Moreover, the way nitrogen adsorption specific surface area uses the rubber constituent which blended the silica bulking agent 100 - 250 m² / g, and whose dibutyl-phthalate oil absorption are 150-250ml / 100g for a tire tread as a bulking agent which replaces the rubber whose glass transition temperature is 0--80 degree C at carbon black by the copolymer of a conjugated-diene compound and 5 - 50% of the weight of an aromatic vinyl compound is indicated by the Europe public presentation patent EPO No. 501227.

[0006]

[Problem(s) to be Solved by the Invention] By the way, the silica restoration combination which makes the solution polymerization diene system polymer obtained considering an organic lithium as an initiator raw material rubber like aforementioned JP,3-252431,A was not enough as processability and abrasion resistance, and, in addition, there was room of improvement by it. Moreover, although the molecular weight of the above-mentioned solution polymerization diene system polymer is increased by making a silane compound into a coupling agent, Mooney viscosity is set as the range [****] and the wear-resistant improvement is aimed at in JP,3-252433,A, examination is hardly made about the requirements for improving the processability of silica combination, for example, the molecular weight distribution of polymer. Furthermore, the problem that carry out breakdown and molecular weight tends to fall although the polymer which carried out distributor shaft coupling using the silane compound does not come out like a tin compound is pointed out conventionally. Moreover, the silica combination like EP No. 0501227 publication is charged without static electricity generated in the automobile escaping on a road surface if a tire tread is constituted from this, since electric insulation is high, and it has the fault of occurring electromagnetic interferences, such as a radio noise. A deer is carried out, and the purpose of this invention has good processability compared with silica restoration combination of this conventional type, and it excels in wet-proof skid nature, low rolling-resistance nature, and abrasion resistance, and is in offering the rubber constituent for tire treads with which sufficient conductivity was moreover secured.

[0007]

[Means for Solving the Problem] When this invention persons constituted the rubber constituent for tires combining the solution polymerization diene system rubber obtained by carrying out distributor shaft coupling by the multifunctional compound [****] containing the diglycidyl amino group as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem, and a silica bulking agent and carbon black, they find out that the desired end is attained and came to complete this invention.

[0008] Namely, the living polymer obtained by this invention making an organic lithium a catalyst in a hydrocarbon solvent, and copolymerizing styrene and 1,3-butadiene Come to carry out distributor shaft coupling by the multifunctional compound containing the diglycidyl amino group. The independence of the distributor-shaft-coupling conversion solution polymerization styrene-butadiene copolymer rubber which whose weight average molecular weight (Mw) is 500,000 or more, and has the molecular weight distribution (Mw/Mn) shown by the ratio of weight average molecular weight (Mw) and number average molecular weight (Mn) in the range of 2.2-3.2, Or the raw material rubber 100 weight section which the remainder becomes from other diene system rubber components is received, including this copolymer rubber 60% of the weight or more. It is related with the rubber constituent for tire treads which makes a silica bulking agent 10 - 80 weight section, and makes carbon black to more than 25 weight sections, and carries out 40 in all to 100 weight section combination of this silica bulking agent and this carbon black, and is characterized by the bird clapper.

[0009] As a multifunctional compound [****] containing the above-mentioned diglycidyl amino group, diglycidyl aniline, a tetraglycidyl ether meta-xylene diamine, tetraglycidyl ether -1, 3-screw aminomethyl cyclohexane, etc. can be illustrated, for example. By choosing suitably the kind (or the number of functional groups) of these multifunctional compounds, the molecular weight of a living polymer, and both reaction mole ratio, the rubber-like polymer adjusted to the molecular weight and molecular weight distribution after a coupling reaction, or the value of a request of the number of unreacted glycidyl groups can be obtained.

[0010] Weight average molecular weight (Mw) is 500,000 or more among the rubber-like polymer obtained in this way, and the styrene-butadiene copolymer rubber which molecular weight distribution (Mw/Mn) are in the range of 2.2-3.2, and contains the unreacted glycidyl group of a piece at least is suitable especially as a rubber component of this invention. The unreacted glycidyl group which remains in this rubber-like polymer raises the interaction of polymer and a silica bulking agent upwards, and is effective, and 500,000 or more and a high thing have advantageous molecular weight (Mw) for a wear-resistant and low febrile improvement. Moreover, they are the requirements to which molecular weight

distribution (Mw/Mn) are indispensable in suppressing the fall of the processability accompanying silica combination or more by 2.2. However, since a heat generation characteristic will fall based on the increase in low-molecular-weight polymer if (Mw/Mn) exceeds 3.2, it is not desirable.

[0011] In order that the distributor-shaft-coupling conversion solution polymerization styrene-butadiene copolymer rubber used in this invention may raise an interaction with a silica further, the feature is in specifying a styrene content and the amount of vinyl combination, and making the pendant machine in a polymer chain increase in addition to the unreacted glycidyl group in a molecule. That is, when setting the amount of vinyl combination of S (mol %) and this butadiene portion to V (mol %) for the styrene content in the polymer chain which constitutes a solution polymerization styrene-butadiene copolymer, especially the thing constituted so that A and B might satisfy simultaneously the relation expressed with a lower formula (1) and (2) is suitable.

$$45 \geq S + 1/2V \geq 25 \quad (1)$$

$$62 \geq S + V \geq 40 \quad (2)$$

In a formula (1), it is difficult for $S + 1/2V$ to make abrasion resistance and a heat generation characteristic good or more by 45, and it cannot maintain wet-proof skid nature or less by 25. Moreover, in a formula (2), if $S + V$ becomes 62 or more, the double bond which can construct a bridge will decrease, a bad influence will appear in vulcanization speed, or less by 40, it becomes insufficient [the amount of pendants] and a strong interaction with a silica cannot be secured.

[0012] In this invention, like the above, it is independent about the conversion solution polymerization styrene-butadiene copolymer rubber which comes to carry out distributor shaft coupling by the multifunctional compound [****], or it is used, blending with other diene system rubber components so that this may be contained 60% of the weight or more in raw material rubber. Interaction with this rate of a blend sufficient between polymer and a silica at less than 60 % of the weight is not acquired, and the desired end is not attained. As other diene system rubber used here, it is [cis- / quantity / natural rubber, a synthetic polyisoprene rubber, and]. -It is / cis- / low / 1, 4-polybutadiene rubber, and]. -The blend rubber which consists of general-purpose diene system rubber, such as 1, 4-polybutadiene rubber, emulsion-polymerization styrene-butadiene copolymer rubber, and solution polymerization styrene-butadiene copolymer rubber, and these one or more sorts can be mentioned.

[0013] The rubber constituent concerning this invention is characterized by carrying out 40 in all to 100 weight section content of this silica bulking agent and the carbon black for a silica bulking agent, including 10 - 80 weight section and carbon black more than 25 weight sections per above-mentioned raw material rubber 100 weight section. Although a silica bulking agent is deficient in the improvement effect of wet-proof skid nature in under 10 weight sections and the total quantity of a silica and carbon black is excellent in rolling-resistance nature in under 40 weight sections, rubber does not have intensity and abrasion resistance is missing. If a silica bulking agent exceeds 80 weight sections or the total quantity of a silica and carbon black exceeds the 100 weight sections, processability and rolling-resistance nature will fall.

[0014] Drawing 1 shows the loadings of carbon black, and a conductive relation about the rubber constituent concerning this invention. A vertical axis is a volume-resistivity value. When there is little carbon black so that more clearly than drawing, about the same electric insulation as silica combination is shown. When a tire was constituted from such combination, static electricity generated in an automobile caused radio-noise generating that it is hard to escape on the ground. Then, in this invention, in order to secure the conductivity of a rubber constituent, carbon black is blended more than 25 weight sections per raw material rubber 100 weight section. Especially the kind of carbon black used here is iodine-adsorption-number (IA) 65 mg/g, although not limited. They are dibutyl-phthalate oil absorption (DBP) of 90cm³ / 100 g above. The reinforcement nature carbon black which shows the above colloidal property can secure abrasion resistance simultaneously with conductivity, and is desirable.

[0015] Moreover, a silica bulking agent has the wet method silica more desirable than a dry-process silica usually known as an object for general rubber. As the suitable example, it is a product made from Japanese Silica. Tradename: Nip seal VN3, AQ, Tokuyama Soda Co., Ltd. make Tradename: TOKUSHIRU U, Shionogi & Co., Ltd. make Tradename: Carplex 1120, product made from Mizusawa

Chemistry Tradename: Siluton R-2 grade can be mentioned.

[0016] In addition, of course to the rubber constituent concerning this invention, a well-known vulcanizing agent, a vulcanization accelerator, a vulcanization promotion assistant, a plasticizer, an antioxidant, a silane coupling agent, etc. can be suitably added besides the above-mentioned component. Also in this case, as for a silane coupling agent, it is desirable to add in 5 - 10% of range of a silica fill according to the usual prescription.

[0017]

[Function] In this invention, the rubber constituent which has low febrility and good abrasion resistance is obtained, without being accompanied by the fall of processability, since the multifunctional compound containing the diglycidyl amino group is used for a coupling agent and the molecular weight and molecular weight distribution are adjusted to the specific range about the styrene-butadiene copolymer rubber combined with a silica. Moreover, the interaction of polymer and a silica can be raised, without having a bad influence on vulcanization speed, since the styrene content and the amount of vinyl combination were set as the specific range and the pendant machine in polymer was made to increase in addition to the diglycidyl amino group which remains into a molecule. Moreover, since specified quantity addition of the carbon black was carried out in addition to the silica, the electric insulation of silica combination is canceled and generating of a radio noise is prevented. By using the rubber constituent of this composition for a tread, it became possible to improve the wet-proof skid nature and rolling-resistance nature of a pneumatic tire, maintaining abrasion resistance.

[0018]

[Example] Below, an example and the example of comparison are given and this invention is explained concretely. Table 1 shows the styrene content (S) of the solution polymerization styrene-butadiene copolymer rubber of each coupling-agent conversion, the amount of vinyl combination of the butadiene section (V), weight average molecular weight (Mw), molecular weight distribution (Mw/Mn), and the amount of pendants (S+V and S+1/2 V).

[0019] About the infrared absorption spectrum by which the microstructure of the styrene-butadiene copolymer rubber in Table 1 is measured using FT-IR, the styrene content was calculated by the Hampton technique, the amount of vinyl combination of the butadiene section was calculated by the MORERO method, and it was determined. Weight average molecular weight (Mw) and molecular weight distribution (Mw/Mn) are the values measured by the gel permeation chromatography by using THF as an expansion solvent.

[0020]

[Table 1]

SBRの種類	A	B	C	D	E	F	G	H
S (モル%)	27.3	12.8	21.9	18.9	7.0	18.9	16.8	14.8
V (モル%)	26.2	32.3	28.9	24.3	33.8	17.0	23.3	39.2
S + 1/2 V	40.5	29.0	35.4	31.1	23.9	27.4	28.5	34.4
S + V	53.5	45.1	50.8	43.2	40.8	33.9	40.1	54.0
Mw (10 ⁻⁴)	68	64	29	70	62	64	61	45
Mw/Mn	3.0	2.6	1.5	3.0	2.5	1.4	2.6	1.4
カップ リング剤	テトラグリシジル メタキシレンジ アミン	テトラグリシジル -1,3-ビス メチルシクロ ヘキサン	トリエトキシシ クロ	テトラグリシジル メタキシレンジ アミン	テトラグリシジル -1,3-ビス メチルシクロ ヘキサン	四酸化ケイ素	テトラグリシジル メタキシレンジ アミン	四酸化スズ

[0021] Cis-[various kinds of distributor-shaft-coupling conversion styrene-butadiene copolymer rubber independence shown in Table 1 or / cis-/ this and] -It came, whenever it was shown in Table 2, and the rubber constituent which makes blend rubber with 1 and 4-polybutadiene rubber (BR01) raw material rubber, and makes emulsion-polymerization styrene-butadiene copolymer rubber (SBR1712) the criteria rubber of characterization was mixed and prepared by the Banbury mixer in the blending ratio of coal.

[0022] Subsequently, since rolling resistance was related to the shearing loss tangent (tan delta) by the following method again in many properties, such as wet-proof skid nature at the time of using for processability and a tire tread about each above-mentioned rubber constituent, abrasion resistance, and conductivity, this was measured and rolling resistance was evaluated.

Processability -- JIS It applies to K6300 correspondingly and is Mooney viscosity. ML 1+4 (100 **) was measured, the case where the value was 80 or less was made into processing fitness (O mark), and the thing exceeding 80 was made into processing difficulty (x mark).

Wet-proof skid nature -- The British Stanley portable skid circuit tester is used for the frictional resistance to the humid road surface which wet the front face of Safety Walk (Type B) by Sumitomo 3 M company with water, and created it. 38 Rubber Chemical and Technology It measured according to the method given in 840 page, and it carried out indexation, having used measured value of the example 1 of comparison as 100, and it considered as the index by which wet-proof skid nature is evaluated. It is so desirable that a value is large.

Rolling-resistance nature -- Made in the Iwamoto factory VISCO ELASTIC SPECTROMETER It is attached to 5mm angle around and a sample with a thickness of 2mm, and is [50Hz and] 5%.

Indexation of the shearing loss tangent (tan delta) measured at the temperature of 60 degrees C was carried out under the shearing condition, having used the example 1 of comparison as 100, and it considered as the index by which rolling-resistance nature is evaluated. In this case, the one where a value is smaller is desirable.

Wear-resistant -- The run bone abrasion tester made from ***** Co. is used, and it is JIS. K6264 is followed and they are 3kg of loads, and 60% of slip ratio. It carried out indexation, having used the example 1 of comparison as 100, and the amount of abrasion losses measured under the condition was made into the index of wear-resistant evaluation. The one where a value is larger is desirable.

Conductive -- When direct current voltage was impressed to inter-electrode [two] on both sides of a

test piece, the current value which passes along a test piece was measured, and the volume-resistivity value (numeric value which ²(ed) voltage with the current which passes along the unit volume of a test piece) which can be found from this was made into the conductive index. The one where a value is smaller is desirable. A result is collectively shown in Table 2.

[0023]

[Table 2]

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5	比較例 6
SBR A	75											
SBR B		75						75				
SBR C									75			
SBR D										75		
SBR E											75	
SBR F												
SBR G			75	75	75	100						100
SBR H												
BR-01 *1	25	25	25	25	25		100	25	25	25	25	
SBR1712 *2												
シリカ (ニガリ AQ)	40	40	15	45	65	65		40	80	40	40	40
カーボンブラック N234	30	30	45	25	25	25		30		30	30	30
N339							80					
S1-69 *3	3.2	3.2	1.2	3.6	5.2	5.2		3.2	6.4	3.2	3.2	3.2
プロセスオイル	30	30	30	30	45	45	37.5	30	30	30	30	37.5
加工性	○	○	○	○	○	○	○	○	○	○	×	×
耐水・耐油・耐薬品性	105	100	100	101	102	105	100	102	101	98	100	106
転がり抵抗性	96	91	97	91	95	96	100	92	97	89	95	93
耐摩耗性	100	114	108	110	113	100	100	91	93	116	101	85
体積抵抗 ($\Omega \cdot \text{cm}$)	10^7	10^7	10^5	10^8	10^8	10^8	10^5	10^7	10^{13}	10^7	10^7	10^7

*1) J S R 社製 シス-ポリブタジエン、*2) 油膜乳化重合 SBR、*3) デグサ社製 シランカップリング剤

[0024] As shown in Table 1 and 2, the rubber constituent (examples 1-6) with which are satisfied of the requirements for composition of this invention like the above is equipped with the wet-proof skid nature and abrasion resistance which have good processability in spite of being silica combination, excel [all] in rolling-resistance nature as compared with the rubber constituent (example 1 of comparison) which consists of an emulsion polymerization SBR of carbon black reinforcement, and are not inferior to this. Moreover, conductivity is also enough.

[0025] Furthermore, when explained in detail, the example 1 of comparison is a rubber constituent for general treads which consists of an emulsion polymerization SBR (SBR 1712) containing carbon black (N-339), and considered this as the control for characterization. Although the example 2 of comparison is the thing of the same combination composition as examples 1 or 2 except having used the solution polymerization styrene-butadiene copolymer rubber which comes to carry out distributor-shaft-coupling conversion by the TORIETOKISHI chlorosilane and rolling-resistance nature and wet-proof skid nature are improved, that molecular weight (Mw) is also as small as 290,000 originates, and it is inferior in abrasion resistance. Moreover, even if it is filling with combination of only a silica bulking agent the requirements for composition raw material rubber starts this invention even if like the example 3 of comparison, electric insulation is high and serves as a constituent in which abrasion resistance was inferior.

[0026] The example with which the example 4 of comparison has the small value of S+1/2 V in the microstructure of the distributor-shaft-coupling conversion solution polymerization styrene-butadiene copolymer rubber concerning this invention, and the requirements for the aforementioned (1) formula

are not filled is shown. In this case, although the greatest effect was acquired about improvement of rolling-resistance nature and abrasion resistance, the improvement effect of wet-proof skid nature is not inferior and desirable. The example 5 of comparison and the example 6 of comparison are examples about the copolymer rubber which carried out conversion by other conventional-type coupling agents (a tetrachlorosilane and tin tetrachloride). Like [rubber / conversion / these] the example 2 of comparison, although an effective effect is accepted in wet-proof skid nature and rolling-resistance nature, since molecular weight distribution (Mw/Mn) are as narrow as 1.4, processability is inferior, and abrasion resistance is bad in especially the latter. This can be considered to originate in molecular weight (Mw) being 500,000 or less independent rubber constituent, excluding a cis-PORIPUTA diene (BR-01).

[0027]

[Effect of the Invention] As above, in this invention, carry out distributor shaft coupling by the multifunctional compound containing the diglycidyl amino group, and it is obtained. Since the specified quantity of a silica bulking agent and carbon black was blended with the raw material rubber which uses the solution polymerization styrene-butadiene copolymer rubber which has a macro and a microstructure, and makes this a principal component and the rubber constituent was constituted, [****] Processability is good, and is excellent in wet-proof skid nature, rolling-resistance nature, and abrasion resistance, and the rubber constituent for tire treads which moreover has conductivity and does not have fear of radio-noise generating is obtained.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About a rubber-like polymer constituent, in detail, this invention has little rolling resistance at low febrility, when it is used for a tire-tread use, and it relates to the rubber-like polymer constituent which brings about the tire tread which unites and has good wet skid resistance ability. *tire tread*

[0002]

[Description of the Prior Art] In recent years, also compared with before, improvement in various performances, such as safety, driving stability, economical efficiency, amenity, and pollution-free nature, is desired with development of an automobile industry to the tire with which an automobile is equipped. Especially, consumption of petroleum system fuel increases by the increase in an automobile, the increase serves as [air pollution substances contained in exhaust gas, such as a carbon dioxide and a nitrogen oxide,] a social problem as pollution, consumption reduction of the petroleum system fuel by the mpg improvement of an automobile and conversion to the electric vehicle which does not take out exhaust gas come to be called for, and the rubber material to which rolling resistance reduces mpg few also into an automobile tire has come to be called for.

[0003] The rolling resistance of a tire is mainly influenced by the hysteresis loss of the tread at the time of tire rotation, and rolling resistance improves by using a constituent with few hysteresis losses. However, as a performance of a tire, safeties, such as driving stability and a brake performance (sentiment skid resistive characteristic) in the wet road surface, endurance ability, such as abrasion resistance, etc. are important performances. However, each of rolling-resistance performances of a tire and sentiment skid resistance ability is performances related to the hysteresis loss of tread rubber, and since these are opposite things, it has been supposed that it is conventionally difficult to improve the both simultaneously. However, since the frequency condition equivalent to the rolling-resistance performance of a tire differs from the frequency condition equivalent to wet skid resistance ability, many attempts which improve these two sorts of performance balance paying attention to the point are made until now.

[0004] Many of these improvement methods are how to carry out improvement in balance of the rolling resistance of a tire, and the wet skid resistance ability by optimizing the raw material rubber which uses carbon black in the tire-tread vulcanized-rubber compound made into a reinforcing filler. For example, the way -50 degrees C or more and a styrene content use [a glass transition temperature] the styrene-butadiene copolymer whose amount of vinyl combination of a butadiene portion is 50 - 80% at 20 - 40% *SBR* for JP,54-62248,A is indicated. However, when such a polymer is used, in order that the rolling-resistance performance and wet skid resistance ability of a tire may use a polymer with high molecular weight low [tensile strength] since they are a high vinyl although it is good, a problem is in processability and a difficulty is in industrial production.

[0005] Moreover, the method using the diene system polymer to which the method using the styrene butadiene copolymer which branched with a specific compound like tin by the high vinyl content to

JP,57-55912,A made benzophenones add at a polymer chain end is indicated by JP,59-117514,A, and it is shown in it that any method has good rolling-resistance performance and wet skid resistance ability of a tire. However, it was raised with the method of improving such rolling resistance, as a trouble that abrasion resistance is not necessarily enough.

[0006] The way rolling resistance also hangs down other good tire performances and a good tire is proposed recently, and the raw material rubber which suits it is also shown by changing into conventional carbon black as a reinforcing filler used for a tire-tread compound to these, and using a silica.

[0007] It compares, when a silica is used as a reinforcing filler and carbon black is used as a general inclination. Although the rolling-resistance performance relevant to febrility-proof or this was good, the hardness and tensile strength of a vulcanized-rubber compound were equivalent and there were troubles, like the shrinkage characteristics of that a form modulus is very low, that abrasion resistance is inferior, that the viscosity of a compound is high, and a compound are large, and processability is inferior. In order to improve the trouble of this silica compound, the method of strengthening the interaction of a silica and rubber using optimization of raw material rubber or a specific organic silane coupling agent etc. is proposed.

[0008] As a method of performing improvement in a performance of the rubber constituent for tire treads which makes a silica a reinforcing filler by improvement of raw material rubber, to JP,62-50346,A After carrying out the polymerization (**) of the diene system monomer by making an organic lithium system compound into an initiator, The rubber constituent for tire treads which uses the rubber containing the specific polymer (**) which the alkoxysilane system compound of specific structure was made to react, and was obtained in the polymerization activity end is indicated, and it is indicated that intensity, abrasion resistance, etc. are improved. Furthermore, it is shown by having the aforementioned specific structure in JP,3-252433,A, and a glass transition temperature facing it a polymer (**) -50 degrees C or more using the rubber constituent for tire treads, and using a silica bulking agent and the silane coupling agent of specific structure for it that a tire with good rolling-resistance performance, wet-proof skid performance, and abrasion resistance is obtained.

[0009] Moreover, the silica bulking agent of the solution polymerization SBR of specific polymer structure and a specific character is used for U.S. JP,5,227,425,B, and the method of bringing about the tire which improves a rolling-resistance performance, abrasion resistance, and a wet-proof skid performance by specifying the kneading conditions of a rubber constituent is proposed. However, also in the technology which uses the silica bulking agent which performed these improvement, the trouble that it was not necessarily enough had processability -- contraction of a rubber constituent is large.

[0010] [Problem(s) to be Solved by the Invention] this invention makes it a technical problem to offer the raw material rubber and the rubber constituent which bring about a good rolling-resistance performance, good abrasion resistance, good wet skid resistance ability, and good processability in the rubber constituent for tire treads which uses a silica bulking agent.

[0011] [Means for Solving the Problem] In order to attain the above-mentioned technical problem, this invention proposes using this rubber-like polymer as a rubber constituent of specific composition further as raw material rubber of the rubber compound for tire treads using the rubber-like polymer of the polymer structure where specification was limited.

[0012] this invention makes the styrene butadiene copolymer rubber obtained by the solution polymerization method which makes an initiator the organic lithium system compound which fulfills the conditions of (A) following (a) - (d) raw material rubber. The 100 weight sections, (a) 25 / 75 - 57/43 (c) glass transition temperature -50 - -10-degree-C (d) Mooney viscosity [the weight ratio of a combined styrene / joint butadiene] [the mole fraction of 1 of the microstructure of 50 / 23/77 - 50(b) butadiene portion, the amount of 2 combination / 1, and the amount of 4 combination] (1+4,100 degree C of ML (s)) are 80-200. (B) a reinforcement nature silica filler 10 - 100 weight (section C) reinforcement nature carbon black The total quantity of the 10 - 100 weight (section D) reinforcement nature silica filler and

Shw
CB

Sx oil

reinforcement nature carbon black a 20 - 100 weight section (G) vulcanizing agent for the extender oil for 0.1 - 20 weight (section F) rubber 1 - 10 weight section [the 60 - 150 weight (section E) organic silane coupling agent] It is the rubber constituent for tire treads to contain.

[0013] moreover this invention by the solution polymerization method which makes an initiator the organic lithium system compound which fulfills the conditions of following (A-1) (a) - (d) The obtained styrene butadiene copolymer rubber is 30 - 95% of the weight of raw material rubber. the mole fraction of 1 of the microstructure of 50 / 23/77 - 50(b) butadiene portion, the amount of 2 combination / 1, and the amount of 4 combination 25 / 75 - 57/43 [the weight ratio of (a) combined styrene / joint butadiene] (c) A glass transition temperature is [-50 - -10 degree-C (d) Mooney viscosity (1+4,100 degree C of ML (s))] 80-200. A polybutadiene rubber (A-2) or the diene system polymer rubber whose glass transition temperature it is styrene-butadiene copolymer rubber whose weight ratios of a combined styrene / joint butadiene are 2 / 98 - 10/90, and is -110--80 degree C -- 5 - 70% of the weight of raw material rubber -- it is (A-1) -- (A-2) 10 - 100 weight (section C) reinforcement nature carbon black for the raw material rubber 100 weight (section B) reinforcement nature silica filler whose weight ratios of the set combined styrene / joint butadiene of the whole raw material rubber are 20 / 80 - 45/55 The 10 - 100 weight section (D) The total quantity of a reinforcement nature silica filler and reinforcement nature carbon black is the rubber constituent for tire treads which contains [the 60 - 150 weight (section E) organic silane coupling agent] 1 - 10 weight section for the extender oil 20 for 0.1 - 20 weight (section F) rubber - a 100 weight sections (G) vulcanizing agent.

[0014] Hereafter, this invention is described in detail. The styrene butadiene copolymer rubber of the raw material rubber which constitutes this invention is the rubber-like copolymer obtained by carrying out the copolymer of styrene and the butadiene by the solution polymerization method which makes an organic lithium system compound an initiator.

[0015] The ranges of the weight ratio of the combined styrene / joint butadiene of this styrene-butadiene copolymer are 23 / 77 - 50/50. If wet skid resistance ability when the amount of combined styrenes has the low tensile strength at the time of silica combination and uses for a tire tread especially at less than 23 % of the weight runs short and the amount of combined styrenes exceeds 50 % of the weight, a degree of hardness will increase and the abrasion resistance of a tire-tread constituent and low-temperature-performance ability will fall sharply. The ranges of the weight ratio of a combined styrene / joint butadiene are 30 / 70 - 45/55 preferably, and the ranges of it are 33 / 67 - 43/57 especially preferably.

[0016] Although styrene can also use in part randomness, a block, or the thing combined with which chain gestalten, such as a block, into the chain of a copolymer if it is the range of the weight ratio of the above-mentioned combined styrene / joint butadiene What does not contain many block styrene with which styrene was connected is desirable in respect of the rolling-resistance nature of a constituent, and it is desirable that the rate of a block of the styrene measured by the part solution method or ozonolysis by the osmic acid is 10 or less % of the weight of the amount of combined styrenes. It is desirable that the amount of the isolation styrene furthermore measured by the ozonolysis is 50% of the weight or more of the amount of combined styrenes in respect of the wet skid resistance ability of a constituent, and the amount of the isolation styrene measured by the ozonolysis is inferior in wet skid resistance ability in 40 or less % of the weight of the amount of combined styrenes.

[0017] The ranges of the mole fraction of 1 of the microstructure of the butadiene portion of the styrene-butadiene copolymer of this invention, the amount of 2 combination / 1, and the amount of 4 combination are 25 / 75 - 57/43.

[0018] In the joint format of a butadiene portion, it is [1 and 2 combination (vinyl combination and homonymy) and / cis-]. -1 [in / this invention / 1, four combination (cis-combination and homonymy), a transformer -1, and four combination (transformer coupling and homonymy) are existed, and] and the amount of 4 combination are. -It is the total quantity of 1, the amount of 4 combination, and the a transformer -1 and the amount of 4 combination. Febrility-proof when 1 and the amount of 4 combination exceeded 75% and 1 and the amount of 2 combination use for a tread constituent at less than 25% is inferior, and on the other hand, if 1 and the amount of 2 combination exceed 57% and 1 and

the amount of 4 combination become less than 43%, the intensity, abrasion resistance, and low-temperature-performance ability of a constituent will get worse extremely. The mole fraction of 1, the amount of 2 combination / 1, and the amount of 4 combination has the desirable range of 27 / 73 - 55/45, and the mole fraction of 1, the amount of 2 combination / 1, and the amount of 4 combination has the still more desirable range of 30 / 70 - 55/45. Each joint format of a butadiene portion can use the thing of various chain gestalten, such as what exists uniformly in a chain, and a thing which increases or decreases along with a chain.

[0019] As a well-known typical method, the styrene-butadiene copolymer of this invention is used into the solvent of hydrocarbon systems, such as a pentane, a hexane, a cyclohexane, benzene, and toluene, as an organic lithium compound or other organoalkali metal compounds, and a polymerization initiator, and is obtained by copolymerizing styrene and a butadiene. The weight ratio of a combined styrene / joint butadiene can be adjusted by the preparation ratio of the styrene of a monomer and the butadiene to be used. In order to consider as the range which specifies the mole fraction of 1 of a butadiene portion, the amount of 2 combination / 1, and the amount of 4 combination by this invention, it becomes possible by adding polar compounds, such as the ether, a polyether, the third class amine, and polyamine.

[0020] When making an organic lithium compound into a polymerization initiator, even if 1 and the amount of 2 combination generally increase, it is [cis- / cis- / 4 combination / / a transformer -1, and]. -

[0021] The range of the glass transition temperature (T_g) of the styrene-butadiene copolymer of this invention is -50--10 degree C. The glass transition temperature specified by this invention is the extrapolation temperature measured using DSC. The glass transition temperature of a styrene-butadiene copolymer is decided by the amount of combined styrenes, and the amount of the joint format (cis-combination, transformer coupling, 1, 2-combination) of a butadiene portion. If the wet skid resistance ability of a tread compound has a low glass transition temperature at less than -50 degrees C and a glass transition temperature, on the other hand, exceeds -10 degrees C, low-temperature-performance ability and abrasion resistance will get worse sharply. The range of a glass transition temperature of -45--20 degree C is desirable.

[0022] In order [which holds the febrility-proof and intensity of a tread compound, and brings about sufficient processability] to bring, the ranges of the Mooney viscosity (1+4, 100 degree C of ML(s)) of the styrene-butadiene copolymer of this invention need to be 80-200. If less than 80 are [Mooney viscosity] insufficient as for febrility-proof, intensity, and abrasion resistance and Mooney viscosity exceeds 200, processability will pose a problem. The range of Mooney viscosity of 80-150 is desirable.

[0023] The styrene-butadiene copolymer rubber of this invention has a desirable thing containing the specific letter polymer molecule of branching, and it contains the letter component of 4 branching obtained by making the compound or tetrachlorosilane which has two diglycidyl amino groups in the styrene butadiene copolymer in which styrene butadiene copolymer rubber has an activity lithium end, and a molecule react ten to 60% of the weight. This specific 4 branching component is effective in order to make the distributed state of a reinforcing agent good, the rubber component of this invention having good few shrinkage characteristics, and as for the amount, it is still more desirable that it is 10 - 40% of the weight of a styrene-butadiene copolymer.

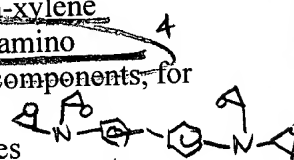
[0024] As a compound which has two diglycidyl amino groups, a tetraglycidyl ether meta-xylene diamine, tetraglycidyl ether 1, 3-screw aminomethyl cyclohexane, a tetraglycidyl ether diamino diphenylmethane, etc. are raised in the molecule used for obtaining 4 specific branching components, for example.

[0025] With an organic lithium system compound, these compounds and tetrachlorosilanes copolymerize styrene and a butadiene and polymerization reaction adds them before a conclusion or a conclusion. In order to control the amount of 4 branching components by this invention in the desirable range, it becomes possible by making the amount of the compound to branch react few to the amount of an activity lithium end.

[0026] Well-known methods, such as a batch process, continuous magnetization methods, or those combination, can be used for the manufacture process of polymer, and the polymer of various kinds of

LIB
Neonpores

used for
branching



Mw/Mn ✓

molecular weight distributions obtained by it can be used for it.

[0027] The molecular weight distribution (ratio of weight average molecular weight (Mw) and number average molecular weight (Mn) (M_w/M_n)) of the styrene butadiene copolymer rubber of this invention have the desirable range of 1.05-4.0. When the styrene butadiene copolymer rubber of this invention contains 4 specific branching components, there is a configuration of molecular weight distribution also with poly modal configurations, such as bimodal one and TORIMODARU, and a bird clapper.

[0028] 5-100 weight section addition of the extender oil for rubber is carried out to the styrene butadiene copolymer rubber 100 weight section, it considers as oil extended rubber, and the styrene butadiene copolymer rubber of this invention can present practical use as carried out in common rubber, and in order to improve processability, considering as oil extended rubber is desirable. The oil exhibition Mooney viscosity (1+4, 100 degree C of ML(s)) at the time of considering as oil extended rubber is a range with desirable 30-80.

[0029] As an extender oil to be used, although the thing of an aromatic system, a naphthene, and paraffin series is used, an aromatic system extender oil is desirable especially. When it considers as oil exhibition polymer, the same with being known for general oil exhibition polymer, Tg of the styrene butadiene copolymer rubber of this invention needs to change according to the amount of an extender oil, and needs to mind the weighted-mean value and bird clapper of Tg of styrene butadiene copolymer rubber, and Tg of an extender oil.

[0030] It sets to the constituent of this invention, and raw material rubber is used in the range of the above-mentioned specific styrene butadiene copolymer rubber (it considers as A-1 component), and other specific conditions of diene system rubber (it considers as A-2 component) specification, blending, using the above-mentioned specific styrene butadiene copolymer rubber independently.

[0031] The diene system rubber of A-2 component blended and used is diene system polymer rubber whose glass transition temperature it is styrene-butadiene copolymer rubber whose weight ratios of a polybutadiene rubber, or a combined styrene / joint butadiene are 2 / 98 - 10/90, and is -110--80 degree C. In these, the so-called high cis polybutadiene rubber which uses the so-called low cis polybutadiene rubber obtained as a polybutadiene rubber by the solution polymerization method which makes an organic lithium system compound a polymerization initiator, a nickel system polymerization initiator, a cobalt system polymerization initiator, or a neodymium system polymerization initiator is usable, and especially, the processability improvement effect at the time of a blend is good, and is desirable. [of a low cis polybutadiene rubber] Moreover, the styrene butadiene copolymer rubber blended and used is the low thing of the amount of combined styrenes, and what is obtained by the solution polymerization method that this also makes an organic lithium system compound a polymerization initiator is desirable.

[0032] The range of the glass transition temperature of A-2 component is -110--80 degree C. It is difficult for a glass transition temperature to obtain low diene system rubber from -110 degrees C, and when a glass transition temperature exceeds -80 degrees C, there are few improvement effects of processability. As for the Mooney viscosity (1+4, 100 degree C of ML(s)) of A-2 component, 25-150 are desirable, and it also uses that to which Mooney viscosity carried out the oil exhibition of the thing of 80-150.

[0033] In this invention, A-1 component and A-2 component are used in the range with which are satisfied that it is the range those weights of whose are A-1/A-2=30-95 % of the weight / 70 - 5 % of the weight, and the weight ratios of the combined styrene / joint butadiene of the whole raw material rubber with which A-1 component and A-2 component were doubled are 20 / 80 - 45/55. If the combined styrene of less than 30 % of the weight or the whole raw material rubber becomes [the amount of A-1 component] less than 20 % of the weight, tensile strength will become low, and if the combined styrene of the whole raw material rubber exceeds 45 % of the weight, low-temperature-performance ability will pose a problem. The weight ratio of the combined styrene / joint butadiene of the whole raw material rubber has the desirable range of 20 / 80 - 40/60.

[0034] In the rubber constituent for tire treads of this invention, a reinforcement nature silica filler is used so that the total quantity of a reinforcement nature silica filler and reinforcement nature carbon black may serve as the 60 - 150 weight section in the 10 - 100 weight section and reinforcement nature

carbon black, using the 10 - 100 weight section. If improvement of a rolling-resistance performance has few amounts of a reinforcement nature silica filler under at 10 weight sections and the 100 weight sections are exceeded, processability will get worse. Since the amount of reinforcement nature carbon black is inferior in the conductive ability of a compound in under 10 weight sections, if static electricity generated by automobile cannot be grounded through a tire and the 100 weight sections are exceeded, processability will get worse. When both total quantity exceeds the 150 weight sections preferably [wet skid resistance ability] under at 60 weight sections, a rolling-resistance performance is inferior.

[0035] The amount of a reinforcement nature silica filler has [the range of 10 - 60 weight section / the range of the 60 - 100 weight section] the range desirable [especially both total quantity] of 20 - 80 weight section in the use than to which the amount of reinforcement nature carbon black attaches greater importance to a rolling-resistance performance. Anything of a wet method silica, a dry-process silica, and a synthetic silicate system silica can be used for the reinforcement nature silica filler used for the rubber constituent of this invention. The high thing of the reinforcement effect is the small silica of a particle diameter, and a granule child and quantity condensation type (a high surface area, high oil-absorption nature) thing has the good dispersibility to rubber, and is desirable especially in respect of physical properties and processability.

[0036] As reinforcement nature carbon black used for the rubber constituent of this invention, it is the object manufactured by the furnace method, and the carbon black whose DBP oil absorption nitrogen adsorption specific surface area is 50-200m² g, and is 80-200ml / 100g is desirable, things, such as FEF, HAF, ISAF, and a SAF class, can be used, and a high condensation type object is especially desirable. Furthermore, it is also possible to use fillers, such as clay, a calcium carbonate, and a magnesium carbonate, if needed with a reinforcement nature silica filler and reinforcement nature carbon black. ✓

[0037] Next, in order to make close a distributor-shaft-coupling operation (cross coupling operation) with a reinforcement nature silica bulking agent and raw material rubber, 0.1-20 weight section combination of the organic silane coupling agent is carried out per raw material rubber 100 weight section at the rubber-like polymer constituent of this invention. Reinforcement nature will be spoiled, if the amount of an organic silane coupling agent has few distributor-shaft-coupling operation effects and exceeds 20 weight sections under in the 0.1 weight section. The amount of an organic silane coupling agent has 5 - 20% of the weight of the desirable range of the amount of a reinforcement nature silica bulking agent.

[0038] As an example of an organic silane coupling agent, a screw-[3-(triethoxy silyl)-propyl]-tetrapod sulfide, a screw-[2-(triethoxy silyl)-ethyl]-tetrapod sulfide, 3-mercapto propyl-trimethoxysilane, 3-triethoxy silyl propyl N, N-dimethylthiocarbamoyl tetrasulfide, 3-triethoxy silyl propyl benzothiazole TETORASURUFIDO, etc. are raised. As for an organic silane coupling agent, a reinforcement nature silica bulking agent, and raw material rubber, in this invention, it is desirable that knead by the 140-180-degree C temperature requirement, and a reinforcement nature silica bulking agent and raw material rubber form sufficient combination.

extender oil [0039] Next, the extender oil for rubber is used for the rubber-like polymer constituent of this invention, and 20-100 weight section combination is carried out per rubber-like polymer 100 weight section. It fluctuates according to the amount of a reinforcement nature silica filler and reinforcement nature carbon black, and the amount of the extender oil for rubber is used so that the elastic modulus of the tread compound after vulcanization may be adjusted. The elastic modulus of a tread compound becomes [the amount of the extender oil for rubber] high too much under in 20 weight sections, driving stability runs short, and if the 100 weight sections are exceeded, febrility-proof will get worse. Especially the amount of the extender oil for rubber has the still more desirable range of 20 - 50 weight section in the pref. use which thinks a rolling-resistance performance as important.

Sx [0040] Next, a vulcanizing agent is used for the rubber-like polymer constituent of this invention in the range of per [1] rubber-like polymer 100 weight section - 10 weight sections. Sulfur is used as a thing typical as a vulcanizing agent, in addition a sulfur content compound, a peroxide, etc. are ***** (ed).

+ accelerators Moreover, it uses together with a vulcanizing agent and amount use of the vulcanization accelerators, such as a sulfenamide system, a guanidine system, and a thiuram system, is carried out if needed.

Furthermore, initial-complement use of a zinc white, stearic acid, a vulcanization assistant, an antioxidant, and the processing aid is carried out for the purpose as a chemical for rubber. add here

[0041] The rubber-like polymer constituent of this invention Raw material rubber, a reinforcement nature silica filler, reinforcement nature carbon black, An organic silane coupling agent, the extender oil for rubber, the chemical for rubber, etc. are kneaded at the temperature of 140-180 degrees C using an internal mixer etc. The performance is demonstrated in the state where it became the vulcanized-rubber compound which furthermore blended a vulcanizing agent, vulcanization accelerators, etc., such as sulfur, using the internal mixer or the roll mill, and was vulcanized at the temperature of 140-180 degrees C after fabrication, and it is used for a tire tread.

[0042] Although the rubber-like polymer of this invention is used suitable for the tire-tread compound which is the gestalt of the vulcanized-rubber compound containing a reinforcement nature silica filler and reinforcement nature carbon black, and makes typical a highly efficient tire and all season tire, it is applicable to other tire uses, a rubber vibration insulator, a belt, an industrial use article, footwear, etc. taking advantage of the feature.

[0043]

[Example] Hereafter, although an example and the example of comparison explain this invention concretely, these do not limit the range of this invention.

[0044] The process of the example SBR of reference : By 10l. of content volume, have an entrance at the pars basilaris ossis occipitalis, and it has an outlet on a head. It is connected with a two-set serial, using as a reactor the autoclave which attached the agitator and the jacket. A metering pump is used from the 1st set of a reactor pars basilaris ossis occipitalis. a butadiene A part for 19.5g/ styrene -- the tetramethylethylenediamine was supplied by part for 0.024g/as 120g a part for /and a polar substance, n-butyl lithium was continuously supplied for 10.5g a part for /and a cyclohexane the speed for 0.0102g/as a polymerization initiator, respectively, and ** in a reactor was held at 97 degrees C a reactor head -- a polymer solution -- continuous -- extracting -- the 2nd set of reactors -- having supplied . The temperature of the 2nd set of reactors was kept at 95 degrees C, 0.3Eq [per one mol of activity polymers] tetraglycidyl ether -1 and 3-screw aminomethyl cyclohexane were added continuously, and the coupling reaction was carried out.

[0045] The styrene butadiene copolymer rubber which has the branching component which removes the solvent after adding an antioxidant continuously in this polymer solution, and is made into the purpose was obtained. Furthermore, in this polymer solution, 37.5 weight sections addition of the aroma tic oil (Japan Energy make X-140) was carried out per polymer 100 weight section, and oil extended rubber (sample 1) was obtained.

[0046] As a result of analyzing, the amount of joint butadienes a sample 1 35% 65%, [the amount of combined styrenes] The microstructure of the butadiene portion for which it calculated and asked according to the Hampton method from the measurement result using the infrared spectrophotometer 1 and the amount of 2 combination are [cis-/ 33% and]. -A transformer -1 and the amount of 4 combination 28% 39%, / 1 and the amount of 4 combination 145 and a glass transition temperature Mooney viscosity (1+4,100 degree C of ML(s)) -33 degrees C, The molecular weight distribution by the GPC measurement (pump : Shimadzu LC- 5A, column:HSG- 40, 50, 60 1 each, a detector : RI) which used THF as the solvent weight average molecular weight (Mw) -- 497,000 and number average molecular weight (Mn) -- 187,000 and molecular weight distribution (Mw/Mn) -- 2.66 -- it is -- the configuration of a GPC curve -- monochrome -- it was modal

[0047] Furthermore, the styrene butadiene copolymer rubber (samples 2-15) from which 1 of the amount of combined styrenes shown in Table 1 and a butadiene portion, the amount of 2 combination, Mooney viscosity, the amount of branched polymers, and a glass transition temperature differ by the method same with having obtained the sample 1 was adjusted. In addition, samples 11-15 are samples for comparison. Moreover, the styrene butadiene copolymer rubber and the polybutadiene rubber of marketing shown in Table 1-2 centering on a thing were also used as a sample.

[0048] The analysis value of the above sample is shown in Table 1-1. In addition, analysis of a sample was performed by the method shown below.

catalyst
polymer is
made
then
absorbed
H₂ into
reactor
Li⁺ end
active
terminator

✓
M weight
Mn/Mw

1) The amount of combined styrenes and the amount sample of joint butadienes were used as the chloroform solution, the amount of combined styrenes [S] (wt%) was measured by absorption of UV254nm by the phenyl group of styrene, and the amount of joint butadienes (wt%) was calculated by calculation as $100 - [S]$.

2) The microstructure sample of a butadiene portion was used as the carbon-disulfide solution, the infrared spectrum was measured in $600-1000\text{cm}^{-1}$ using the solution cell, and the microstructure of a butadiene portion was searched for according to the formula of the method of Hampton from the predetermined absorbance.

[0049] 3) Use a glass transition temperature DSC and measure by part for 10 degrees-C/of programming rates. Extrapolation start temperature (On setpoint) was set to Tg.

4) The GPC measurement curve of the sample before the amount branching reaction of branched polymers and the branched sample was measured (the measurement conditions of GPC are the same as the above-mentioned determination of molecular weight), and the amount of branched polymers was calculated from both configuration.

[0050] The rubber compound was obtained by the following kneading method using the combination shown in Table 2 by making into raw material rubber the sample shown in one to examples 1-10 and example of comparison 10 Table 1-1 and 1-2.

[0051] The [kneading method] pressurized kneader (0.3l. of *****) is used. Raw material rubber, a filler, (a silica and carbon black), a silane coupling agent, aromatic oil, a zinc white, and stearic acid are kneaded (mixing-time 6 minutes, the highest attainment temperature of 170 degrees C). In addition, the combination which contains a silica as a filler kneaded again the compound obtained above after cooling to the room temperature (mixing-time 5 minutes, the highest attainment temperature of 170 degrees C). An antioxidant, sulfur, and a vulcanization accelerator are kneaded with the open roll set as 80 degrees C after cooling. This was cast, it vulcanized with the vulcanizing press for [160 degrees-C] 25 minutes, and the performance of physical properties which shows the following tire performances was measured.

[0052] 1) Compound Mooney viscosity : use a Mooney viscometer and measure at 100 degrees C. Forge-fire processability good 2 mill contraction with a small value: Use the 6 inches roll mill set as 50 degrees C. A roll gap is set to 0.2mm and judged with the shrinkage characteristics of the sheet which carried out sheeting. An object with less contraction is better. O Display in four stages of O**x. O is ***** at best. x is the worst and it is contraction large 3 hardness: JIS. K6301 It measured with the JIS-A hardness meter.

4) Tensile strength : JIS It measures by the tension test method of K6301.

5) Impact resilience : JIS The impact resilience of K6301 is measured at 70 degrees C. The mpg performance of the one where a number is larger is good.

[0053] 6) Febrility-proof : use a good rich flexometer. Difference ΔT of rotational frequency 1800rpm, 0.225 inches of strokes, the load of 55pound, the start temperature of 50 degrees C, and the temperature of 20 minutes after and start temperature is measured.

7) Wet skid resistance ability : use a viscoelasticity spectrometer (made in the Iwamoto factory), and compute from the value of T_{Δ} measured on 10Hz, 0 degree C, and the conditions of **1% of *****. A performance is so good that a value is large.

[0054] 8) Abrasion resistance : measure using a pico abrasion tester. It is wear-resistant good, so that a value is large. The measurement result of a performance is shown in Table 3. Moreover, wet skid resistance ability and wear-resistant balance are shown for the balance of wet skid resistance ability and impact resilience in drawing 2 at drawing 1.

[0055] The constituent of combination of specific silica content using the styrene butadiene copolymer rubber limited by this invention of an example 1 - an example 10 shows good processability, impact resilience, febrility-proof, grip performance, and abrasion resistance. On the other hand, impact resilience, febrility-proof, and abrasion resistance are inferior in the constituent of the examples 1, 2, and 3 of comparison of combination of only carbon black. Moreover, the constituent of the example 9 of comparison which used the sample 11 - the sample 15, and emulsion polymerization SBR of polymer structure from which it separates from the range of limitation of this invention of the example 4 of

comparison - the example 8 of comparison, and the example 10 of comparison has the performance item which is not enough, and is not desirable.

[0056] The rubber-like polymer shown in Table 1-2 as a component (A-2) was used, using the samples 1, 3, 6, and 10 of the specific styrene butadiene copolymer rubber of 11 to examples 11-21 and example of comparison 15 this invention as a component (A-1), it considered as the rubber constituent like the example 1 by the combination shown in Table 4, and the performance was measured. Wet skid resistance ability and wear-resistant balance are shown for the result in Table 4 at drawing 3. Within the limits of the kind of the component (A-1) limited by this invention, and component (A-2), and a composition ratio, as shown in Table 4, the balance of abrasion resistance and wet skid resistance ability is improved sharply.

[0057] The constituent was obtained like the example 1 using the sample 1 of the specific styrene butadiene copolymer rubber of 16 to examples 22-24 and example of comparison 18 this invention by combination which is [loadings / carbon black / the silica loadings shown in Table 2,] different. The result is shown in Table 5. It is shown in Table 5. The constituent of a good ** ratio within the limits shows good processability, impact resilience, febrility-proof, grip performance, and abrasion resistance with the silica loadings and carbon black loadings which are limited by this invention.

[0058]

[Table 1]

表 1 - 1

試料 番号	結合ス チレン 量 (wt%)	結合ブ タジエ ン量 (wt%)	ブタジエン部分ミクロ構造			ガラス 転移温度 T _g (On set) (°C)	分岐		ムーニー 粘度 (ML1+4, 100°C)	油展ポリマー	
			1, 2 結合量 (% in BD)	1, 4 シス 結合量 (% in BD)	1, 4 トランス 結合量 (% in BD)		分枝剤 *	分岐ポ リマー 量 (%)		油展量 (重量部)	ムーニー 粘度 (ML1+4, 100°C)
1	35	65	33	28	39	-33	TGAMH	25	145	37.5	60
2	40	60	38	26	36	-23	TGAMH	20	135	37.5	55
3	35	65	45	23	32	-28	TGAMH	25	133	37.5	53
4	42	58	30	29	41	-25	SiCl ₄	25	135	37.5	57
5	25	75	33	28	39	-48	SiCl ₄	35	131	37.5	52
6	25	75	55	19	26	-31	TGAMH	20	133	37.5	50
7	30	70	40	25	35	-35	SiCl ₄	15	123	37.5	50
8	35	65	33	28	19	-33	-	0	112	37.5	41
9	47	53	27	31	42	-23	TGAMH	25	130	37.5	55
10	43	57	40	25	35	-17	TGAMH	25	138	37.5	55
11	35	65	23	32	45	-41	TGAMH	30	130	37.5	55
12	30	70	60	17	23	-21	SiCl ₄	50	135	37.5	50
13	21	79	57	18	25	-36	TGAMH	20	135	37.5	51
14	20	80	40	25	35	-49	TGAMH	25	130		50
15	35	65	33	28	39	-33	TGAMH	15	70	37.5	28

*〔分岐剤〕 TGAMH: テトラグリシジル-1,3-ビスアミノメチルシクロヘキサン、 SiCl₄: 四塩化ケイ素

[0059]
[Table 2]

表 1 - 2

試料 番号	試 料 名	結合スチ レン量 (wt%)	結合ブタ ジエン量 (wt%)	ブタジエン部分ミクロ構造			ガラス 転移温度 T _g (on set) (°C)	油 展 ポ リ マ ー	
				1, 2 結 合 量 (%in BD)	1, 4 シ ス 結 合 量 (%in BD)	1, 4 ト ラ ンス 結 合 量 (%in BD)		油 展 量 (重量部)	ムーニー 粘度 (ML1+4, 100°C)
16	SBR1712	23.5	76.5	17	13	70	-56	37.5	52
17	SBR5820	31	69	17	13	70	-47	37.5	55
18	ジエン531	0	100	13	35	52	-95	37.5	42
19	JSR BR31	0	100	2	96	2	-108	37.5	35
20	試作溶液重合SBR	10	90	13	35	52	-86	37.5	45

*1 油展ムーニー粘度:

アロマチックオイルを重合体100重量部あたり37.5重量部添加した油展重合体のムーニー粘度

[0060]
[Table 3]

表 2 (表中の数字の単位はすべて重量部)

配 合 名	S - 1	S - 2	S - 3	S - 4	R - 1	R - 2	R - 3	R - 4
ゴム状重合体 合計量	100	100	100	100	100	100	100	100
アロマチック油 *1	37.5	37.5	37.5	60	37.5	37.5	37.5	15
シリカ *2	60	65	25	60	0	75	60	45
カーボンブラックN339*3	10	5	47	-	75	0	15	11
カーボンブラックN234*4	-	-	-	34	-	-	-	-
カーボンブラックN330*5	5	5	3	6	-	-	-	4
カーボンブラック合計量	15	10	50	40	75	0	15	15
シランカップリング剤 *6	5	5	3	5	0	8	0	4
亜鉛華	3	3	3	3	3	3	3	3
ステアリン酸	2	2	2	2	2	2	2	2
老化防止剤3c *7	1	1	1	1	1	1	1	1
ワックス	1	1	1	1	1	1	1	1
硫黄	1.5	1.5	1.5	1.8	1.5	1.5	1.5	1.5
促進剤CZ *8	1.5	1.5	1.5	1.7	1.5	1.5	1.5	1.2
促進剤D *9	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.2

*1: ジャパンエナジー (株) 製 商品名: ソニックス X-140 *2: 日本シリカ (株) 製 商品名: ニブシールAQ
 *3: 東海カーボン (株) 製 商品名: シーストKH *4: 東海カーボン (株) 製 商品名: シースト7H
 *5: Degussa 社製 シランカップリング剤含有マスターバッチ X-50S (商品名) 中に含まれるカーボンブラック
 *6: Degussa 社製 シランカップリング剤含有マスターバッチ X-50S (商品名) 中に含まれるカーボンブラック
 物質名: ビス-[3-(トリエトキシシリル)-プロピル] - テトラスルフィド
 *7: 物質名 N-イソプロピル-N'-フェニル-2-ベンゾチアジルスルフェニルジアミン
 *8: 物質名 N-シクロヘキシル-2-ベンゾチアジルスルフェニルジアミン
 *9: 物質名 ジフェニルグアニジン

[0061]
[Table 4]

表 3 - 1

	試料 番号	配合名	加 工 性		加 硫 物 性 能					
			配合物 ムーニー度 粘 (MJ1+4, 130℃)	ミル 収縮 評価	硬さ (JIS-A)	引張強度 (MPa)	反発弾性 70℃ (%)	耐発熱性 ΔT (℃)	ウェット スエッジ 抵抗性能 (指数)	耐摩耗性 (指数)
比較例 1	1	R-1	60	○	67	20.8	45	35	100	100
実施例 1	1	S-1	78	◎	68	26.8	60	27	100	130
実施例 2	2	S-1	74	◎	69	26.8	59	26	105	125
実施例 3	3	S-1	73	◎	68	25.2	59	29	102	128
実施例 4	4	S-1	77	○	71	27.2	58	28	104	127
実施例 5	5	S-1	72	○	67	25.5	62	28	91	140
実施例 6	6	S-1	72	◎	70	23.5	58	27	101	123
実施例 7	7	S-1	70	○	68	26.1	60	27	98	133
実施例 8	8	S-1	66	○	70	25.5	57	30	100	125
実施例 9	9	S-1	76	○	72	25.9	57	30	104	122
実施例 10	10	S-1	73	○	73	25.1	57	29	108	120

[0062]

[Table 5]

表 3 - 2

	試料 番号	配合名	加工性		加 硫 物 性 能					
			配合物 ムーニー度 粘 (ML1+4, 130℃)	ミル 収縮 評価	硬さ (JIS-A)	引張強度 (MPa)	反発弾性 70℃ (%)	耐発熱性 ΔT (℃)	ウェット スキッド 抵抗性能 (指数)	耐摩耗性 (指数)
比較例 2	2	R-1	63	○	69	20.4	42	35	106	92
比較例 3	5	R-1	58	○	68	21.3	49	34	93	115
比較例 4	11	S-1	84	△	71	26.1	57	36	95	128
比較例 5	12	S-1	76	×	70	24.5	55	30	107	110
比較例 6	13	S-1	72	△	69	21.7	57	30	99	116
比較例 7	14	S-1	74	△	67	22.3	61	29	88	130
比較例 8	15	S-1	54	○	68	22.1	53	35	100	118
比較例 9	16	S-1	65	×	69	27.5	56	37	85	124
比較例 10	17	S-1	64	×	68	29.5	55	36	92	115

[0063]

[Table 6]

表 4

	試料					配合名	加工性		加硫物性					性能	
	A-1成分		A-2成分		全体の結合スチレン量(重量%)		配合物ムーニー度(ML1+4, 100℃)	ミル収縮評価	硬さ(JIS-A)	引張強度(MPa)	反発弾性70℃(%)	耐発熱性ΔT(℃)	ウェットスキス抵抗性能(指数)	耐摩耗性(指数)	
	番号	重量部	番号	重量部											
実施例 1	1	100	-	-	35	S-1	78	◎	68	26.8	60	27	100	130	
実施例 11	同上	90	18	10	31.5	S-1	85	◎	68	25.2	60	28	98	140	
実施例 12	同上	70	同上	30	24.5	S-1	90	◎	69	23.5	58	30	94	178	
比較例 11	同上	50	同上	50	17.5	S-1	95	○	69	19.7	57	33	85	190	
実施例 13	同上	70	19	30	24.5	S-1	87	◎	69	23.5	59	30	91	160	
実施例 14	同上	70	20	30	27.5	S-1	84	◎	69	24.2	58	30	95	167	
比較例 12	同上	70	18	30	24.5	R-1	83	○	71	19.8	47	39	94	135	
実施例 15	3	70	同上	30	24.5	S-1	85	◎	69	23.3	58	29	96	171	
実施例 16	同上	70	19	30	24.5	S-1	83	◎	69	22.7	59	29	90	165	
実施例 17	6	80	18	20	20.0	S-1	82	◎	69	22.2	60	28	95	144	
比較例 13	同上	70	同上	30	17.5	S-1	85	○	69	19.8	60	30	92	143	
実施例 18	10	60	18	40	25.8	S-1	79	◎	71	24.5	57	31	98	156	
実施例 19	同上	60	19	40	25.8	S-1	83	◎	71	24.7	56	31	95	150	
実施例 20	同上	60	20	40	29.8	S-1	80	◎	71	26.2	57	30	97	152	
実施例 21	同上	35	同上	65	21.6	S-1	88	○	70	22.5	58	33	87	185	
比較例 14	同上	20	同上	80	16.6	S-1	95	△	70	19.3	57	35	80	200	
比較例 15	12	70	19	30	21.0	S-1	81	△	71	20.3	58	28	90	136	

[0064]
[Table 7]

表 5

	試料	充 填 材			加工性	加 硫 物 性 能						
		配合名	シリカ重量部	カーボンブラック配合重量部		配合の特徴	配合物ムーニー度 (ML1+4, 100℃)	硬さ (JIS-A)	引張強度 (MPa)	反発弾性 70℃ (%)	耐発熱性 ΔT (℃)	ウェットスリップ抵抗性能 (指数)
比較例16	1	R-2	75	0	シリカのみ	90	69	25.7	62	27	98	105
比較例17	1	R-3	60	15	シランカップリング剤なし	120以上	77	22.4	51	50以上	95	70
実施例22	1	S-2	65	10		82	68	26.5	60	26	99	125
実施例1	1	S-1	60	15		78	68	26.8	60	27	100	130
実施例23	1	S-3	25	50		71	68	24.6	55	30	102	120
比較例1	1	R-1	0	75	カーボンブラックのみ	60	67	20.8	45	35	100	100
実施例24	1	S-4	60	40	アロマチック油=60部	80	71	25.2	52	33	110	130
比較例18	1	R-4	40	15	アロマチック油=15部	120以上	73	22.5	65	25	90	130

[0065]

[Effect of the Invention] By using the styrene-butadiene copolymer rubber of the specific structure of this invention by the specific combination containing a reinforcement nature silica filler and reinforcement nature carbon black, processability, a rolling-resistance performance, a grip performance, and the wear-resistant good rubber constituent for tire treads are offered. This rubber constituent for tires is useful as a material of the automobile tire which needs a rolling-resistance performance.

[Translation done.]

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* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the rubber constituent for tire treads which raised the place on the snow of the pneumatic tire suitable for a run of a place on the snow or a freezing road surface, especially a tread portion, and the road surface retention span in a freezing road surface.

[0002]

[Description of the Prior Art] In order to run a snow-and-ice road surface, the studless tire has spread instead of the spike tire made to generate dust pollution. In connection with it, the automobile accidents which a freeze road surface appears and consider a slip as a cause occur frequently, it has social-problem-ized and the studless tire which raised the braking nature in Hikami is called for strongly on the large day of temperature.

[0003] In order to heighten the method and the drainage effect which add the matter (a mineral, an animal fiber, vegetable matter, etc.) for digging up the method and the ice road surface which attain rationalization of the combination which attains rationalization of rubber, such as a method and a vulcanizing agent, as a means for raising, the braking nature, i.e., the road surface retention span, in a snow-and-ice road surface of a studless tire, the method of carrying out minute foaming etc. combines, and is enforced.

[0004] If a cis polybutadiene rubber is used for the rubber for studless tires, although the Hikami performance will be raised about raw material rubber, on a full freeze road surface, degradation is caused, and although the road surface retention span in a snow-and-ice road surface improves, by natural rubber, it has the fault to which the road surface retention span in the usual humid road surface falls. On the other hand, in order to maintain the rubber elasticity in low temperature, the low polymer of a glass transition point is used, or the method (JP,60-137945,A) using the softener of the low melting point for raising an ice road surface and friction, the method (JP,6-263921,B) of rationalizing monomer composition and a microstructure, etc. are examined. However, while these rubber raises low-temperature-performance ability, processability, rolling resistance, etc. are sacrificed, and it cannot be said that the military requirement is satisfied enough.

[0005]

[Problem(s) to be Solved by the Invention] Now, improvement in the performance in which that to which the studless tire raised further the braking performance in a snow-and-ice road surface is demanded, and, in addition, also included the retention span in rolling-resistance nature, processability, and a humid road surface is needed. However, the rubber constituent which fills these enough is not obtained yet.

[0006]

[Means for Solving the Problem] As a result of repeating examination to meet the request, by using it combining the styrene-butadiene random copolymer, natural rubber, and butadiene rubber which have the styrene-butadiene random copolymer, the natural rubber, or the specific polymer structure of having specific polymer structure as raw material rubber, this invention persons are epoch-makingly excellent

in low-temperature-performance ability, and complete this invention which consists of a working characteristic, low rolling-resistance nature, and a rubber constituent for tires that raised the retention span in a humid road surface.

[0007] The amount of vinyls of the butadiene section this invention three to 9% of the weight Namely, 18 - 29%, [(A) styrene content] Distributor shaft coupling is carried out by the coupling agent of three or more functionality, and the Mooney viscosity before distributor shaft coupling (ML1+4;(100 degrees C) I) is [the Mooney viscosity after 10-30, and distributor shaft coupling (ML1+4;(100 degrees C) C)] 30-80. The ratios (C/I) of the Mooney viscosity before and behind distributor shaft coupling are 1.5-5. As opposed to the raw material rubber 100 weight section which a molecular-weight-distribution pattern becomes from monochrome modal styrene-butadiene random-copolymer 10 - 90 weight sections, and (B) natural rubber 90 - 10 weight sections The rubber constituent for studless tire treads, [0008] which are characterized by carrying out 5-50 weight section addition combination of 10 - 80 weight section and the softener for carbon black The amount of vinyls of the butadiene section three to 9% of the weight And 18 - 29%, [(A) styrene content] Distributor shaft coupling is carried out by the coupling agent of three or more functionality, and the Mooney viscosity before distributor shaft coupling (ML1+4;(100 degrees C) I) is [the Mooney viscosity after 10-30, and distributor shaft coupling (ML1+4;(100 degrees C) C)] 30-80. The ratios (C/I) of the Mooney viscosity before and behind distributor shaft coupling are 1.5-5. As opposed to the raw material rubber 100 weight section which a molecular-weight-distribution pattern becomes from monochrome modal styrene-butadiene random-copolymer 10 - 90 weight sections, and (B) natural rubber 90 - 10 weight sections, and (C) butadiene rubber 1 - 50 weight sections It is related with the rubber constituent for studless tire treads characterized by carrying out 5-50 weight section addition combination of 10 - 80 weight section and the softener for carbon black.

[0009] The styrene-butadiene random copolymer which constitutes this invention is explained in detail below. A styrene content is [3 - 9 % of the weight and a butadiene content] 97 - 91 % of the weight, especially preferably, a styrene content is 5 - 9 % of the weight, and the butadiene content of a styrene-butadiene random copolymer is 95 - 91 % of the weight. Since intensity when a styrene content considers as this invention constituent at less than 3 % of the weight falls, Tg will go up and a low-temperature property will fall if 9 % of the weight is exceeded, it is not desirable. Moreover, styrene needs to be carrying out the polymerization in the state of the random chain into the chain of a copolymer. styrene -- a block -- or since the impact resilience and low-temperature property of a constituent will fall if the polymerization is carried out to the block for the part, it is not desirable

[0010] In the joint format of the butadiene section, it is [cis-]. -1 and 4 combination (cis-combination), a transformer -1 and four combination (transformer coupling), and 1 and 2 combination (vinyl combination) exist. The amount of vinyls is defined as the content of the vinyl combination to the total quantity of cis-combination, transformer coupling, and vinyl combination. The amount of vinyls of the butadiene portion in the styrene-butadiene copolymer which constitutes this invention is restricted to 18 - 29%. If the amount of vinyls exceeds 29%, Tg of a styrene-butadiene copolymer will become high, the degree of hardness in the low temperature of this invention constituent will rise, and the Hikami performance will fall at less than 18%. Being distributed uniformly is desirable although vinyl combination of a butadiene portion may increase or decrease along with a chain even if it exists uniformly in a chain.

[0011] Moreover, the styrene-butadiene random copolymer which constitutes this invention Distributor shaft coupling of the styrene-butadiene random copolymer which has an activity end is carried out by the coupling agent of three or more functionality. The Mooney viscosity before distributor shaft coupling (ML1+4;(100 degrees C) I) is [the Mooney viscosity after 10-30, and distributor shaft coupling (ML1+4;(100 degrees C) C)] 30-80. the ratio (C/I) of the Mooney viscosity before and behind distributor shaft coupling -- 1.5-5 -- it is -- a molecular-weight-distribution pattern -- monochrome -- a modal thing is required

[0012] It is required to have the branching structure which carried out distributor shaft coupling by the coupling agent of three or more organic functions in order to acquire the low-temperature-performance ability and the processability of a rubber constituent of this invention. The styrene-butadiene random

copolymer obtained by the coupling agent of two organic functions is not easy to carry out a cold flow, and inferior to physical properties, and desirable. Furthermore, since the efficiency of elevation of polymer solution viscosity to a coupling reaction will become bad if the amount of the coupling agent used increases from the need that Mooney viscosity ML 1+4 (100 degrees C) before distributor shaft coupling makes the rate of distributor shaft coupling high less than by ten and 30 is exceeded preferably economically, it is not desirable.

[0013] If sufficient intensity cannot be discovered but 80 is exceeded when Mooney viscosity ML 1+4 (100 degrees C) after distributor shaft coupling is used as a constituent less than by 30, processability will decrease and industrial use will become difficult. It is small, and the effect of distributor shaft coupling needs to raise coupling-reaction efficiency for the thing exceeding 5 considerably, and the ratio (C/I) of the Mooney viscosity before and behind distributor shaft coupling does not have it at less than 1.5. [industrially desirable] If the molecular-weight-distribution pattern measured by GPC does not come out modally [monochrome], the outstanding low-temperature-performance ability is not obtained.

[0014] As long as the styrene-butadiene random copolymer which constitutes this invention is a copolymer applicable to the above-mentioned specific structure, the manufacture method may be what thing. The typical manufacture method of obtaining these copolymers is shown below.

[0015] A styrene-butadiene random copolymer is set in inert solvents, such as a hexane, a cyclohexane, and benzene. The need is accepted using an organic lithium or other alkali metal compounds, such as n-butyl lithium, as a polymerization catalyst. as a co-catalyst component As a compound which adjusts the amount of vinyl combination if needed further using the organic compound which makes organic acid chloride, such as alkoxides, such as potassium butoxide, a dodecylbenzenesulfonic-acid salt, and a sodium stearate, the example of representation It is obtained by copolymerizing the butadiene and styrene of a monomer by the predetermined ratio using polar organic compounds, such as the ether, a polyether, a tertiary amine, polyamine, a thioether, and hexamethylphosphortriamide. The amount of vinyl combination is controllable by the addition and polymerization temperature of the aforementioned polar organic compound. Moreover, in the aforementioned polymerization method, various compounds, such as acetylene, 1, 2-butadiene, a fluorene, a primary amine, and a secondary amine, can also be used as a molecular weight modifier.

[0016] Next, distributor shaft coupling of the copolymer chain which has the activity end obtained above is carried out, and the styrene butadiene copolymer which constitutes this invention is obtained. As a coupling agent, the polyfunctional compound of three or more organic functions of the poly epoxy compounds, such as halogenated compounds, such as a silicon tetrachloride, methyl 3 silicon chloride, ethyl 3 silicon chloride, butyl 3 silicon chloride, a tin tetrachloride, methyl 3 tin chloride, ethyl 3 tin chloride, and butyl 3 tin chloride, tetraglycidyl ether -1, 3-screw aminomethyl cyclohexane, tetraglycidyl ether -1, 3-screw amino diphenylmethane, epoxidation soybean oil, and a liquefied epoxidation polybutadiene, is mentioned. The copolymer of the letter of branching or a radial is obtained by the coupling reaction.

[0017] Moreover, it is possible to use together the activity end of a polymer and the functional-group content compound (modifier) which reacts with a coupling agent, and to also make it react to a polymer end. Specifically, modifiers, such as a little salt-ized tin compound, a carbonyl compound, an amino-group content benzophenone compound, an isocyanate compound, and a phosphate compound, are used. It is a little salt-ized tin compound preferably and they are triphenyl a little salt-ized tin, trimethyl a little salt-ized tin, tributyl a little salt-ized tin, etc.

[0018] Both a batch process continual processes and those combination can be used for the polymerization process which obtains the above-mentioned polymer. Moreover, if the copolymer of the above-mentioned specific structure is obtained even if based on the method or emulsion-polymerization method which uses the Ziegler type catalyst which consists of organic compounds, such as other polymerization methods except using a lithium catalyst, for example, nickel, cobalt, and titanium, and organic-metal components, such as a lithium, magnesium, and aluminum, any polymerization method of a copolymer is usable.

[0019] It is a means indispensable to the purpose which raises a low-temperature property, abrasion resistance, and processability to blend and use the styrene-butadiene random copolymer and natural rubber which were mentioned above for the raw material rubber which constitutes the constituent of this invention. Styrene-butadiene random copolymers are [10 - 90 weight section and the natural rubber of a blend ratio] 90 - 10 weight sections. Since processability will fall if a styrene-butadiene random copolymer cannot discover a road surface retention span, the low-temperature-performance ability, i.e., the freezing road surface, which is the feature of this invention constituent under in 10 weight sections, but 90 weight sections are exceeded, it is not desirable. Preferably, a styrene-butadiene random copolymer is 30 - 80 weight section, and natural rubber is 70 - 20 weight section.

[0020] Furthermore, it is also possible to blend and use the styrene-butadiene random copolymer, natural rubber, and butadiene rubber which were mentioned above for the raw material rubber which constitutes the constituent of this invention. The elastic modulus in low temperature can be lowered by blending butadiene rubber. For a styrene-butadiene random copolymer, 10 - 90 weight section and natural rubber are [90 - 10 weight section and the butadiene rubber of a blend ratio] 1 - 50 weight sections. Since $\tan \delta$ near [which is the feature of this invention] -30 degree C will decrease and low-temperature-performance ability will fall if the amount of blends of butadiene rubber exceeds 50 weight sections, it is not desirable. If it is the object usually used, the butadiene rubber which constitutes this invention may especially be what kind of object, and will not be limited.

[0021] The carbon black which constitutes this invention will not be limited especially if generally used for a tire use. As a concrete form, the furnace black of SAF, ISAF, and HAF and FEF etc. can be used. The small carbon black of a particle is desirable in physical properties, and the dispersibility to rubber is also good and that of a granule child and quantity condensation type (a high surface area and quantity oil-absorption nature) thing is still more desirable especially in respect of physical properties and processability.

[0022] The amount of carbon black is 10 - 80 weight section need to the raw material rubber 100 weight section. It is 50 - 75 weight section preferably. If 80 weight sections are exceeded, since a degree of hardness will become high, elongation will also decrease, a good rubber property will be lost, and reinforcement effect sufficient in under 10 weight sections will not be acquired but intensity will fall, it is not desirable.

[0023] The initial complement of the softener which constitutes the constituent of this invention is 5 - 50 weight section to the raw material rubber 100 weight section. Since a long-term hardness change becomes remarkable and low-temperature-performance ability stops being discovered with time when 50 weight sections are exceeded, preferably, under in 5 weight sections, processability falls, kneading of rubber, carbon black, etc. becomes very difficult, and a uniform constituent is no longer obtained. A paraffin series process oil, a naphthene process oil, and a aromatic-series (tic [an aroma]) system process oil are used for a softener.

[0024] As a vulcanizing agent of the constituent of this invention, sulfur, a sulfur-chloride compound, an organosulfur compound, etc. can be used. The initial complement of a vulcanizing agent is 0.1 - 10 weight section to the raw material rubber 100 weight section. If below the 0.1 weight section and 10 weight sections are exceeded, good rubber elasticity will not be discovered. In addition, it is also possible to use together a vulcanization accelerator and a cross linking agent. As a vulcanization accelerator, compounds, such as a GUAJININ system, an aldehyde-amine system, an aldehyde-ammonia system, a thiazole system, a sulfenamide system, a thiourea system, a thiuram system, a dithio carbamate system, and a xanthate system, can be used. As a cross linking agent, an oxime compound besides radical generating agents, such as an organic peroxide compound and an azo compound, a nitroso compound, and a polyamine compound can be used.

[0025] Moreover, it is also possible to add a reinforcing agent, a bulking agent, a vulcanization assistant, a coloring agent, a flame retarder, lubricant, a foaming agent, a plasticizer, processing aid, an antioxidant, an antioxidant, a scorch retarder, an ultraviolet-rays inhibitor, an antistatic agent, a coloring inhibitor, an adhesion promoter, other compounding agents, etc. if needed.

[0026] As an additive for a snow-and-ice road surface scratching and making an effect discover, it is

also possible to add a metal, sand, a mineral, glass, a glass fiber, an animal fiber, vegetable fiber, the vegetable matter, etc.

[0027] As a reinforcing agent of others which are added if needed, organic reinforcing agents, such as inorganic reinforcing agents, such as a silica and an activation calcium carbonate, and high styrene resin, phenol-formaldehyde resin, are used, and these inorganic or organic reinforcing agents are used below in 80 weight sections to the raw material rubber 100 weight section. Moreover, in order to combine these reinforcing agents and raw material rubber, it can also be used combining adhesion promoters (coupling agent), such as a silane system compound. As a bulking agent, a calcium carbonate, clay, talc, an aluminum hydroxide, a zeolite, the diatom earth, an aluminum sulfate, a barium sulfate, etc. can be used.

[0028] As an antioxidant or an antioxidant, amine derivatives, such as a diphenylamine system and a p-phenylene diamine system, a quinoline derivative, a hydroquinone derivative, monochrome phenols, diphenols, thio bisphenols, hindered phenols, and phosphorous acid ester can be used, per raw material rubber 100 weight section, 0.001-10 weight section addition is carried out, and these can also use two or more sorts together. A well-known thing can be used for the rubber combination chemical of an ultraviolet-rays inhibitor, lubricant, a foaming agent, a foaming assistant, a flame retarder, an antistatic agent, a coloring inhibitor, and others according to the purpose of use.

[0029] The rubber constituent of this invention is vulcanized, after mixing raw material rubber and various compounding agents and fabricating subsequently to the target configuration with the various mixed equipments generally used for mixture of a rubber constituent, for example, an open roll, a Banbury mixer, a kneader extruder, etc. Taking advantage of the feature, the rubber constituent of this invention is suitable for a studless tire, and more specifically fits the tread section of a studless tire, the cap tread section, and the under-tread section.

[0030]

[Example] Hereafter, although an example and the example of comparison explain this invention concretely, these do not limit the range of this invention.

[0031] The process of an example of reference 1 styrene-butadiene random copolymer (S-1) : With [of 10l. of content volume] an agitator, Connect with a two-set serial by using an autoclave with a jacket as a reactor, and a metering pump is used from the 1st set of a reactor pars basilaris ossis occipitalis. A part for 1.5g/, and n-hexane for 28.5g a part for /and styrene A part for 120g/, [a butadiene] The tetramethylethylenediamine was supplied by part for 0.01g/as a polar substance (vinylation agent), n-butyl lithium was continuously supplied the speed for 0.012g/as a catalyst, respectively, and ** in a reactor was held at 100 degrees C. From the curing-units head, the polymer solution was extracted continuously and the 2nd set of reactors was supplied. It added continuously to the 2nd set of reactors, and the coupling reaction of the 0.5Eq [per one mol of activity polymers] silicon tetrachloride was carried out to them. 0.5 section addition of the 2 and 6-G tert-butylhydroxytoluene was carried out per polymer 100 section as an antioxidant at the obtained styrene-butadiene copolymer, and the solvent was removed. The analysis value of the obtained copolymer S-1 is shown in Table 1.

[0032] The process of a styrene-butadiene random copolymer (S-2-4, R-1-4): The styrene-butadiene copolymer was obtained on the same conditions as S-1 except changing the addition, using a tetramethylenediamine as the addition of a styrene monomer, and a vinylation agent. The analysis value of the obtained copolymer is shown in Table 1.

[0033] The process of a styrene-butadiene random copolymer (S-5-7, R-5-6): The styrene-butadiene copolymer was obtained on the same conditions as S-2 except having used a tin tetrachloride (S-5), ethyl 3 silicon chloride (S-6), tetraglycidyl ether -1, and 3-screw aminomethyl cyclohexane (S-7) as a coupling agent. The analysis value of the obtained copolymer is shown in Table 1.

[0034] The process of a styrene-butadiene random copolymer (R-7-9): R-7 lowered the addition of a coupling agent, and decreased the ratio of Mooney viscosity ML 1+4 (100 degrees C) before and behind distributor shaft coupling. R-8 obtained the copolymer with a bimodal molecular-weight-distribution pattern with a blend. R-9 used emulsion-polymerization SBR#1502 (Japan Synthetic Rubber Co., Ltd. make) of marketing as it was. The analysis value of a copolymer is shown in Table 1.

[0035] The styrene content of a copolymer, the amount of vinyls of a butadiene portion, Mooney viscosity, and the molecular-weight-distribution pattern were measured by the method shown below.

1) The microstructure styrene-butadiene copolymer of a styrene content and a butadiene portion was dissolved in the carbon disulfide, with the infrared spectrophotometer, the infrared absorption spectrum was measured and SHISU of a styrene content and the butadiene section, the transformer, and the amount of combination of a vinyl were calculated by the Hampton method.

2) Mooney viscosity ML 1+4 (100 degrees C)

The L type rotor was used and Mooney viscosity was measured at 100 degrees C.

3) The molecular-weight-distribution pattern sample was used as the THF solution, and the chromatogram was measured in GPC (pump : LC[by Shimadzu Corp.]- 5A, a column : polystyrene gel HSG- 40, 50, 60 1 each, a detector : differential refractometer). The molecular-weight-distribution pattern was determined from the configuration of a chromatogram.

[0036] It kneaded by the combination and the kneading method of showing below the styrene-butadiene random copolymer (S-1) manufactured in the example 1 of example 1 reference, and vulcanization fabrication was carried out for 20 minutes, and 160 degrees C of various physical properties were measured. About this result, it is ** to Table 2.

[0037] [Combination]

A styrene-butadiene copolymer 50 weight sections natural rubber 50 weight sections carbon black *1 45 weight sections aroma oil 5 weight sections zinc white 5 weight sections stearin acid 2 weight section antioxidant (810NA) *2 1 weight section (vulcanization-accelerator CZ) *3 1 weight section sulfur 1.7 weight section *1N339 : SHISUTO KH nitrogen adsorption specific surface area of 93m by Tokai Carbon Co., Ltd. 2 / g, DBP oil absorption 119ml/100g*2 N-isopropyl-N'-phenyl-p-phenylene diamine Ouchi Shinko Chemical -- NOKURAKKU 810made from Industry-NA*3 N-cyclohexyl -- NOKURAKKU CZ made from -2-benzo thiazyl Sulfenamide Ouchi Shinko Chemical Industry [0038] The [kneading method] Carbon black, aroma oil, a zinc white, stearin acid, and the antioxidant were kneaded to the styrene-butadiene copolymer in the Banbury mixer (capacity of 1.7l., temperature of 160 degrees C). Sulfur and the vulcanization accelerator were kneaded with an open roll (10 inches, 80 degrees C).

[Vulcanization molding] The constituent was put into metal mold, with a 160-degree C press, pressurization heating was carried out for 20 minutes, and vulcanization molding was carried out.

[0039] Each performance of the vulcanizate shown in Table 2 was measured as follows.

1) Hardness : JIS-K -6301 It is based on an JIS-A hardness tester.

2) Tensile strength, elongation-after-fracture:JIS-K -6301 It is based on a tension test method.

3) Impact resilience : in 70-degree-C oven, after the 1-hour preheating, the RYUPUKE method by JIS-K -6301 and the sample were taken out quickly, and were measured. Impact resilience serves as an index with which rolling resistance is expressed and fuel-efficiency is expressed. It excels in fuel-efficiency, so that a numeric value is large.

[0040] 4) Wet skid resistance : use the portable skid circuit tester of Stanley London, use Safety Walk (three em company make) as a road surface, and it is ASTM. It measured according to the method of E303-83. It is the index of the grip property in the wet road surface, and it is so desirable that a numeric value is large.

5) Compound Mooney viscosity : it measured at 100 degrees C using the L type rotor. If a numeric value value exceeds 80, it will be hard coming to process it, and will be hard coming to also treat that too small.

[0041] 6) Abrasion resistance : ASTM According to D2228-83, it measured using the pico abrasion tester. A result is expressed with a relative value, and it is so good that a numeric value is large. [of abrasion resistance]

7) Viscoelastic property : storage-modulus E', loss-modulus E'', and tandelta were measured on the frequency of 10Hz by the viscoelasticity spectrometer (made in the Iwamoto factory). Low-temperature-performance ability had small E' in -30 degrees C, and tandelta evaluated it noting that the large direction was the performance which raises the braking nature in Hikami.

[0042] Except having used the styrene-butadiene random copolymer (S-2-7, R-1-9) manufactured in examples 2-7, the example 1 of comparison - the example 1 of 8 reference, after obtaining a rubber constituent on the same conditions as an example 1, various physical properties were measured. A result is shown in Table 2. Low-temperature-performance ability was summarized to drawing 1.

[0043] The rubber constituent was obtained by the same combination as an example 1 except having used the raw material rubber composition shown in Table 3 using the styrene-butadiene random copolymer (S-2) manufactured in examples 8-10, the example 11 of comparison - the example 1 of 13 reference. These physical-properties results are shown in Table 4. Low-temperature-performance ability was summarized to drawing 2.

[0044]

[Table 1]

表 1

試料 番号	スチレン-ブタジエン共重合体						分子量分布 パターン
	スチレン 含量 (wt%)	ブタジエン部 のビニル結合 (%inBD)	カップリング剤	カップリング前 ML1+4(100℃) I	カップリング後 ML1+4(100℃) C	C/I	
R-1	2	23	SiCl ₄	15	58	3.9	モノモーダル
S-1	5	24	SiCl ₄	17	59	3.5	"
S-2	8	23	SiCl ₄	17	60	3.5	"
R-2	13	24	SiCl ₄	16	60	3.8	"
R-3	8	13	SiCl ₄	18	61	3.4	"
S-3	8	19	SiCl ₄	19	60	3.2	"
S-4	8	28	SiCl ₄	19	59	3.1	"
R-4	8	33	SiCl ₄	16	60	3.8	"
S-5	8	23	SnCl ₄	16	59	3.7	"
S-6	8	23	SiCl ₃ Et	19	50	2.6	"
S-7	8	23	TGAMH *	18	62	3.4	"
R-5	8	23	SiCl ₂ Et ₂	18	38	2.1	"
R-6	8	24	なし	58	—	—	"
R-7	8	24	SiCl ₄	30	42	1.4	"
R-8	8	23	SiCl ₄	12	41	3.4	バイモーダル
				23	80	3.5	(ブレンド)
R-9	23.5	19	なし	52	—	—	モノモーダル

*テトラグリシジル-1, 3-ビスアミノメチルシクロヘキサン

[0045]

[Table 2]

表 2

	共重合体 試料番号	硬 さ (JIS-A)		引張強度 (MPa)	$E' \times 10^{-3}$ dyn/cm ² -30℃	tan δ -30℃	リュブケ 反発弾性 70℃ (%)	ウエット スキッド 抵抗	配合物 ML1+4 (100℃)
		23℃	-30℃						
比較例1	R-1	62	73	19.1	2.3	0.27	72	45	65
実施例1	S-1	62	73	24.2	2.4	0.34	70	48	64
" 2	S-2	62	73	26.5	2.5	0.36	69	50	65
比較例2	R-2	62	75	26.2	4.2	0.35	67	51	63
" 3	R-3	62	73	26.4	2.4	0.26	71	47	65
実施例3	S-3	62	73	25.7	2.4	0.33	70	48	64
" 4	S-4	62	73	24.3	2.6	0.36	68	51	66
比較例4	R-4	62	73	23.8	3.0	0.28	67	52	65
実施例5	S-5	62	75	27.0	2.5	0.36	71	50	59
" 6	S-6	62	73	24.0	2.5	0.38	70	50	63
" 7	S-7	62	73	26.5	2.7	0.35	71	50	67
比較例5	R-5	63	74	22.0	4.3	0.30	67	49	80
" 6	R-6	62	74	25.2	3.9	0.25	69	50	82
" 7	R-7	62	74	23.8	3.8	0.29	67	49	52
" 8	R-8	62	73	24.5	3.9	0.28	68	50	58
" 9	R-9	62	76	25.7	5.2	0.27	63	55	65

[0046]

[Table 3]

表 3

	原料ゴム (重量部)		
	共重合体 S-2	天然ゴム	* ポリブタジエン
比較例10	5	95	0
実施例 8	30	70	0
" 2	50	50	0
" 9	70	30	0
比較例11	95	5	0
実施例10	60	30	10
比較例12	20	10	70
比較例13	0	70	30

*BR-01 (日本合成ゴム (株) 製)

[0047]

[Table 4]

表 4

	硬 さ (JIS-A)		引張強度 (MPa)	$E' \times 10^{-8}$ dyn/cm ² -30℃	tan δ -30℃	リュブケ 反発弾性 70℃ (%)	ウェット スキッド 抵抗	配合物 ML1+4 (100℃)
	23℃	-30℃						
比較例10	62	75	28.1	4.5	0.35	67	52	56
実施例 8	62	73	27.0	3.5	0.36	68	51	61
" 2	62	73	26.5	2.5	0.36	69	50	65
" 9	62	72	25.3	2.0	0.36	70	50	67
比較例11	62	71	24.0	2.0	0.36	71	50	75
実施例10	62	71	27.5	1.5	0.33	71	49	68
比較例12	60	71	25.1	2.4	0.25	71	48	70
" 13	61	71	25.7	2.5	0.25	68	48	66

[0048]

[Effect of the Invention] By using the constituent which consists of the styrene-butadiene random copolymer of this invention, natural rubber, carbon black, and a softener, it excels in a low-temperature property and processability extremely, and low rolling-resistance nature and the rubber constituent for tire treads also with the good retention span in a humid road surface are obtained. This rubber constituent is useful as a material of the studless tire which needs the Hikami performance.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

see
NS

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to an acrylonitrile-butadiene rubber constituent. It is related with the acrylonitrile-butadiene rubber constituent which does not contain a sulfur component at all and which can be vulcanized in more detail.

[0002]

[Means for Solving the Problem] According to this invention, the rubber constituent which blends the compound containing two or more epoxy groups, (b) (c) Chisso, or phosphorus compounds, and is characterized by the bird clapper and which can be vulcanized is offered to the rubber 100 weight section which consists of (a) acrylonitrile-butadiene rubber 0 - the 95 weight sections, and acrylonitrile-butadiene rubber 100 with a carboxyl group - 5 weight sections in this way.

[0003]

[Problem(s) to be Solved by the Invention] As a result of inquiring wholeheartedly, when vulcanizing acrylonitrile-butadiene rubber with a carboxyl group by the epoxy compound, this invention person etc. finds out the rubber constituent and bird clapper which were excellent in the oil resistance which does not contain a sulfur component at all, and came to complete this invention based on this knowledge.

[0004]

[Description of the Prior Art] Acrylonitrile-butadiene rubber is rubber which was excellent in thermal resistance and oil resistance, employs the feature efficiently and is used for oil seal, O-ring, packing, the gasket, etc.

[0005] Generally as the vulcanization method of acrylonitrile-butadiene rubber, there is scorch time, and the sulfur vulcanization in which short-time vulcanization is possible is used. However, for the use in electronic equipment, a vulcanization system in which the sulfur compound in a vulcanizing agent or a vulcanization accelerator may have a bad influence, and does not contain a sulfur component at all is desired. Although there is vulcanization by organic peroxide as a vulcanization system which does not use sulfur, there are troubles, such as a lapse of a moldability and organic peroxide.

[0006]

[Embodiments of the Invention] The acrylonitrile-butadiene rubber used in this invention is the copolymer of acrylonitrile and a butadiene, and 25% or more of acrylonitrile is desirable from the field of oil resistance.

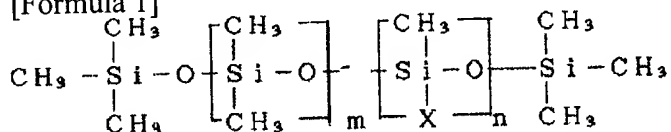
[0007] The acrylonitrile-butadiene rubber with the carboxyl group used in this invention's is acrylonitrile, a butadiene, and the copolymer with a cull BOKIRU machine of a monomer, and 25% or more of acrylonitrile is desirable from the field of oil resistance. As a monomer with a carboxyl group, an acrylic acid, a methacrylic acid, etc. are mentioned, for example.

[0008] The above-mentioned acrylonitrile-butadiene rubber and acrylonitrile-butadiene rubber with a carboxyl group are blended so that the carboxyl group in the rubber 100 weight section may contain 0.01-0.2 mols. If [above-mentioned] the number of mols of a carboxyl group is within the limits, it does not necessarily need to blend acrylonitrile-butadiene rubber. Preferably, a carboxyl group is 0.02-

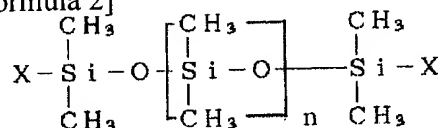
0.08 mols to the rubber 100 weight section.

[0009] As a compound with the epoxy group beyond (b)2 piece used in this invention, the addition product of polyfunctional alcohols, such as ethylene glycol, a propylene glycol, a diethylene glycol, a polyethylene glycol, a polypropylene glycol, a trimethylol propane, and a glycerol, and the GURINJIRU ether is mentioned, for example. Moreover, epoxy resins, such as the bisphenol A type, a phenol novolak type, a biphenyl type, and an alicyclic type, are also mentioned. Moreover, for example, an epoxy denaturation silicone oil which is expressed with a formula 1 and a formula 2 is also mentioned.

[Formula 1]

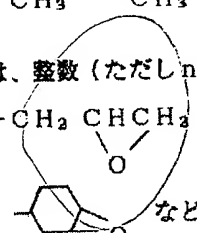


[Formula 2]



n, m は、整数（ただし $n \geq 2$ ）

X は、 $-\text{CH}_2 - \text{CH}(\text{O}) - \text{CH}_2 -$

$-\text{CH}_2 -$  などのエポキシ基を含有する置換基

[0010] To the rubber 100 weight section, preferably, an epoxy group blends the 0.005-0.2 mols of the above-mentioned epoxy compounds so that 0.01-0.8 mols may be contained. (c) Chisso or phosphorus compounds used in this invention is used as a vulcanization accelerator. Specifically, nitrides, such as phosphorus compounds, such as a triphenylphosphine, triphenyl benzyl FOSUFONIUMU chloride, and a tetrabutylphosphonium star's picture, a tetrabutyl ammonium star's picture, a lauryl trimethylammonium star's picture, triethyl octyl ammoniumchloride, a triethylenetetramine, and o-Trilby guanidine, etc. are mentioned. the amount used -- the rubber 100 weight section -- receiving -- a 0.01mm mol - 20mm mol -- it is a 1mm mol - 10mm mol preferably By the amount used fewer than a 0.01mm mol, vulcanization cannot produce efficiently late. Moreover, even if it blends more mostly than a 20mm mol, the further facilitatory effect cannot be found.

[0011] The rubber constituent obtained by this invention blends arbitrarily the compounding agent usually used for rubber, and can carry out the thing of it. For example, lubricant, processing aid, a plasticizer, and an antioxidant can be blended in order to improve processability, flexibility, and thermal resistance. Moreover, carbon black, a silica, clay, etc. can be used as a reinforcing agent and a bulking agent. These may be carrying out surface treatment. Moreover, a pigment and a coupling agent can also be blended. Since the carboxyl group of acrylonitrile-butadiene rubber and the epoxy group of an epoxy compound form a bridge formation chain, the rubber constituent obtained by this invention does not need a required compounding agent, i.e., sulfur, a vulcanization accelerator, a vulcanization assistant, organic peroxide, a polyfunctional joint use bridge agent, etc., when usually vulcanizing acrylonitrile-butadiene rubber.

[0012] Especially the method of preparation of the rubber constituent of this invention does not have limitation, can add a component arbitrarily in the first half, and can mix it with the usual kneading machines, such as a kneader, a Banbury mixer, and an open roll. Thus, the rubber constituent of this invention obtained can be vulcanized on the conditions for about 2 minutes - 30 minutes with the temperature of 150 degrees C - 200 degrees C. Moreover, you may perform secondary vulcanization at the same temperature if needed.

[0013]

[Example]

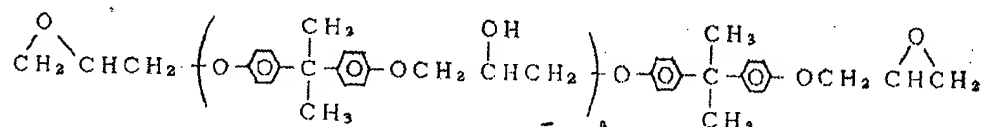
[Example] Although an example is given to below and this invention is explained to it still more concretely, this invention is not limited to this example. In addition, the section is weight criteria as long as there is no notice especially.

After mixing polymer and a compounding agent with an open roll by combination prescription shown in an example and the example table 1 of comparison, press cure was performed for 10 minutes at 170 degrees C. Subsequently, JIS Many physical properties of each vulcanizate were measured according to K-6301, and the value was shown in Table 2.

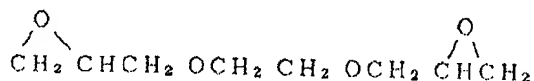
	実施例 1 *1	実施例 2 *1	実施例 3 *1	比較例
日本ゼオン(株)製コップール1042	50	60	50	100
日本ゼオン(株)製DN1072	50	40	50	-
MAFカーボン	-	-	40	40
シリカ	40	40	-	-
ステアリン 酸	1	1	1	1
ハ ラフィン135° F	1	1	1	1
4,4'-(α , α -ジメチルベンジル)ジフェニルアミン	1	1	1	1
油化シェルエポキシ(株)製エポコート604 *2	2.5	-	-	-
エチレングリコールジグリシジルエーテル *3	-	3	-	-
油化シェルエポキシ(株)製エポコート828 *2	-	-	3.5	-
ラウリルトリメチルアンモニウムブ ヲマイト	1	-	1	-
テトラブ チルホスフォニウムブ ヲマイト	-	1	-	-
硫黄	-	-	-	0.5
ジ ヘンゾ チアジ ルジ スルファイト	-	-	-	1.5
テトラメチルチウラムジ スルファイト	-	-	-	1.5

*1 二次加硫: 130°C×2時間

*2



*3



[0014] Table 1.

試験項目	実施例 1	実施例 2	実施例 3	比較例
常態物性値				
硬度(JIS-A)	72	71	72	68
引張強度(kgf/cm ²)	183	157	158	196
伸び(%)	300	240	300	430
熟老化試験 (130℃×70時間、オープン中)				
硬度変化(pts)	+ 3	+ 2	+ 5	+ 7
引張強度変化率(%)	-30	-32	+22	+14
伸び変化率(%)	-47	-44	-42	-45
耐油性試験 (JIS No. 3油中130℃×70時間)				
硬度変化(pts)	- 7	- 9	- 8	- 7
引張強度変化率(%)	-23	-23	-20	-28
伸び変化率(%)	-17	-25	-28	-30
体積変化率(%)	+15.6	+18.9	+15.1	+16.0
耐圧縮永久歪 (130℃×70時間、オープン中)				
	38	40	30	34

[0015] Table 2.

[0016]

[Effect of the Invention] Since it has good oil resistance, although it can be used for oil seal, O-ring, packing, a gasket, etc. taking advantage of this performance, since the vulcanized rubber manufactured by this invention in this way does not contain a sulfur component at all in a rubber constituent, it is useful to a seal of electronic equipment with which the sulfur component contained in rubber does a bad influence, especially O-ring, etc.

[Translation done.]